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WOOL GROUP MEETING*

MILTON HARRIS

Presiding

CHAIRMAN HARRIS: Within the last few years, at several annual meetings, a series of very interesting papers dealing with the approaches to dyeing problems have been initiated by Drs. Kienle, Royer, McCleary and others. In these papers they have applied some rather interesting techniques and principles to the theoretical and fundamental aspects of dyeing. I am glad to note that many of the tests they have developed for measuring depths of color and penetration are now applied quite widely in many textile mills.

Therefore, I think it very fortunate that we have a continuation of that series of papers. Dr. Kienle this morning is going to discuss the effects of variations in wool on its dyeing. Of course, as every dyer knows, everything that has happened before the cloth or fabric reaches the dye house is always blamed on the dyer, but any of these treatments may affect the dyeing.

Dr. Kienle! (Applause)

. . . Dr. Kienle presented his prepared paper . . . (Applause).

WOOL DYEING:
Effect of Variations in Wool*

R. H. KIENLE, G. L. ROYER and H. R. McCLEARY

Presented by R. H. Kienle

BECAUSE wool is biological in origin, there are variations in its formation and composition, not inherent in other fibers, which affect its dyeing. These natural variations are due to animal breed and atmospheric conditions during the growth of the wool. To these variations must be added changes in character due to physical and chemical processing before dyeing. It has been found that quantitative dye-exhaustion studies and microscopical examination of the wool itself are very useful in determining the extent of any change which has taken place in wool. In this paper, some of the effects upon dyeing caused by variations existing in natural wool will be discussed and this will be followed by an examination of the effect of various wool processing operations upon the dyeing.

Dyeing and staining procedures have been suggested as methods for determining damage or changes in the wool fiber[1]. In many of these tests, the stain is not necessarily characteristic of the chemical change in the wool, but is dependent upon the rate at which the dye is taken up by the wool. It is to be expected that variations in wool itself will affect the dyeing and it is known that certain of the processing operations change the wool so as to affect subsequent dyeing. These variations in the wool affect the application of some dyes more than others. Every dye is a different chemical compound and as such will have its own individual dyeing characteristics. Conclusions drawn from a study of one dyestuff cannot be extended to include all dyestuffs. In this study, we have chosen dyes whose rate of exhaustion is known to be affected by certain variations in the wool fibers. While the same dye was not used in all of the studies, as many of the comparisons as possible were made with the same dye and dyeing conditions. It should, therefore, be remembered that the conclusions obtained by the dye and dyeing procedure used in the examples do not necessarily warrant similar conclusions with other dyes. However, the technique used for the determination of dyeing rates can readily be used with the other dyes and dyeing processes.

Another paper to be published by our research laboratory will describe the technique for measuring the exhaustion rate in an instrument called the "Dyeometer." In general, the technique consists of measuring the color characteristics of the dye bath during the dyeing operation by the use of a recording spectrophotometer or a recording colorimeter[2]. The dye bath is controlled so as to reproduce as nearly as possible the variables which enter into the dyeing operation. These are: temperature, time, rate of moving the fabrics in the dye bath, volume of the dye bath, etc. The material being dyed is mounted on a stirrer either in the form of skeins or raw stock which is turned at a constant rate in the dye bath. The volume of the dye bath is kept constant by use of a condenser which returns all vapors from the dye bath. The heat is provided electrically by a nichrome wire coil and the temperature is controlled by a mercury thermoregulator. The dye itself is circulated through the dye bath past the thermoregulator and through a glass cell in which it can be examined at all times during the dyeing operation. This circulation is carried out by means of a nitrogen gas-lift so that the dye bath is in continuous circulation through the material being dyed and the use of the inert gas for the circulation minimizes any decomposition of the dyestuff. The insertion of the dye cell, through which the dye bath is continuously circulating, into the spectrophotometer or colorimeter makes possible measurements on the dye bath at any interval. From the photometric recording thus obtained, the dye strength of the bath may be calculated at any time during the dyeing operation. Changes in shade are also detectable from the spectral curve and this is quite useful in the interpretation of the dyeing operation. The per cent dye bath strength is plotted against time and thus dye exhaustion curves for the dyeing operation are obtained. The experimental error for the dye bath exhaustion plots is probably not greater than ±3% at any time, based on the initial dye bath strength.

The pH of the dye bath is known to be a factor which affects the rate of dyeing. In the dyeing studies described in this paper, the pH of the dye bath was controlled by carrying out the dyeings in buffered solutions. Since the same pH has not been chosen for all experiments, an untreated skein was dyed under the same conditions as the skein whose dyeing rate characteristics was being investigated. Each of the variations which we have studied will be discussed under a separate heading and the treatment of the wool before dyeing and the dyeing conditions will be described.

* Presented at Annual Meeting, Atlantic City, N. J., October 14, 1944.

It should not be concluded that a change in the rate of dyeing necessarily indicates any "damage" to the wool. Whewell and Austerlitz[1] have discussed the measurements of damage by existing methods and state that the task of finding a suitable method depends upon the definition of "damage." From their point of view the term damage is "reserved for the assessment of the desirable and undesirable properties of the material." This paper will use dyeing rate data not as a measure of damage but only to indicate the effect of various factors on dyeing. No attempt has been made to discuss each factor in detail but certain observations on the effect of these factors in dyeing are reported.

VARIATIONS IN COMMERCIAL FABRICS

To show the wide variation in wools, four samples of woolen piece goods of similar construction were purchased on the open market. The previous history of these pieces is not known. They were ready for sale as undyed wool piece goods. These samples were dyed at 95°C. with 3% Calcomine Fast Red 8B at a bath ratio of 80 to 1. Each bath was buffered to a pH of 4.2 with an acetate buffer. This particular dyestuff was selected because it is one which dyes quite fiber-unlevel on wool and tends to show up any differences in the wool. Plots of the dye bath exhaustion curves are shown in Graph 1 and it can be seen that there is a very marked difference in the rates of dyeing.

The presence of grease or oil on wool has an influence on the rate of dyeing as will be discussed in another section of this paper and to prove that this was not a factor causing the differences in these samples, all four of the samples were extracted with ether and then dyed. There was only a minor effect upon the rate of dyeing.

The microscopical examinations of the cross sections showed the fibers to be about the same diameter eliminating fiber size as a cause of the differences in dyeing rate. The microscopical examination for fiber levelness showed that Sample 2, which dyed most rapidly, had the best fiber levelness while Sample 1 had the poorest. This indicates that the differences in the dyeing rate of the four fabrics was caused by the wool fibers used in their construction.

Wool being a natural fiber is subject to many variations before it is cut from the sheep's back and it is well known that wool is very heterogeneous. It is true that a great deal is accomplished in the sorting and classifying of wool but it is impossible to make an exact classification because of the variation which may exist from end to end of the same fiber.

EFFECT OF WEATHERING

The Wyoming Experimental Station at Laramie, Wyoming, under the direction of Robert H. Burns, in cooperation with the Cotton Processing Division of the Southern Regional Laboratory of the U. S. Department of Agriculture, carried out experiments on sheep of the Seaverson Live Stock Company to study the effect of weathering on wool during growth. Experiments were carried out on sheep which were covered with cotton coats and on control sheep in the same flock which were unprotected. It is not the purpose of this article to discuss the advantages and disadvantages of this procedure but it has been found that wool grown under such coats, designated as rugged wool, has improved properties. Samples of various grades of wool both rugged and unrugged were dyed in the Dyeometer. The exhaust rate curves shown in Graph 2 show that the unrugged wool dyes faster than the rugged wool. Microscopical examinations showed that the fiber size of these two samples were approximately the same and that the fiber levelness was better on the unrugged sample (Figure 1 rugged, Figure 2 unrugged). The dyestuff used was 2 per cent Calcofast Orange 4R, a research dye which is known to differentiate between various types of wool. Dyeings were carried out at a pH of 6 in buffered dye baths at the boil. Before dyeing, the wool was boiled for ½ hour in a pH 6 buffer to bring it to a definite pH. The dyeing rate curves and the microscopical examination showed that covering of the wool during the growing period produced a wool which dyed slower indicating less weathering. It may be questioned whether the increased quality of wool produced is of value from an economic viewpoint; nevertheless these experiments prove that exposure to weather and light does affect the dyeing rate.

EXPOSURE TO LIGHT

Exposure of wool to light while on the back of the sheep is important relative to the nature of the wool fiber which is produced. Any subsequent exposure of wool is also important. For this reason, it is known that redyeing of exposed wool fabrics offers some difficulty in that the dyeing characteristics are changed after exposure. Light has been known also to cause streaks and differences in dyeing on the ends of rolls which have been stacked so as to be exposed to light. In order to show that light exposure had a definite effect upon the rate of dyeing, 5-gram skeins of wool were exposed in the Fade-Ometer for various periods of time. Graph 3 shows the dyeing rate curves for 2% dyeings of Calcomine Fast Red 8B carried out at 95°C. in baths buffered at a pH of 4.2. It is evident that light exposure increases the rate of dyeing. Microscopical examination shows that when fibers are exposed to light a much larger per-

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Harold R. McCleary was born in Huntsville, Ohio, October 11, 1913. He was educated in the public schools of Bellefontaine, Ohio, and then attended Monmouth College, Monmouth, Illinois, where he received the B.S. degree in 1937 with honors magna cum laude. He attended the graduate school of Columbia University and received the Ph.D. degree in chemistry in 1941. Since that time he has been employed by the Calco Chemical Division, American Cyanamid Company, Bound Brook, New Jersey, where he is now an Assistant Chief Chemist in the Physical Chemical Research Department engaged in kinetic studies relating to dyestuffs and textile materials.

George L. Royer, born at Akron, Ohio, January 28, 1908. A. B. Akron University, 1929; Ph.D. Cornell University, 1932. Assistant Director of Physical Chemical Research, Calco Chemical Division, American Cyanamid Company, Bound Brook, N. J., in charge of Dyeing and Mrcroscopical Units. Member of Am. Chem. Soc.; Microchem. Soc.; Am. Inst. Chem.; Optical Soc.; Am. Assoc. Textile Chem. & Colorists; Soc. Dyers and Colorists; Amer. Assoc. Textile Technologists; New York Microscopical Soc.; Biol. Photog. Assoc. Specialization and publication in the following fields:— Micro-Analytical Chemistry; Microscopy; Spectroscopy; Dyeing; Colloidal Chemistry; Photography.

centage dye heavily, indicating that the dye can penetrate much more rapidly into the fibers after the light exposure than before.

EFFECT OF FIBER SIZE

The size of the fiber, which in reality means the surface area, affects the rate of dyeing to a marked extent. This is shown in Graph 4 where the rate curves for the dyeings of 36s and 64s wool are plotted, the dyeings being carried out with Calcocid Blue Black ex. conc. (C.I. 246) at the boil in a bath buffered at pH 5. It is apparent that the 64s dyed at a more rapid rate than the 36s. While there may be some differences in the nature of the wool itself, the greater surface area of the 64s produced a more rapid rate of exhaustion. In this particular experiment, the equilibrium exhaustion for the 64s was greater than that for the 36s so it is suspected that these two wools were not of exactly the same chemical nature in that they do not take up the same amount of dye at equilibrium exhaustion. In considering the color reflected from these two different sizes, one must bear in mind that equal dye concentrations on the two size fibers will not show the same color value. This phenomenon has been discussed in a previous paper[3].

EFFECT OF HEAT

In the drying of wool, the temperature of the dryer is of no importance until after all the moisture has been evaporated from the material; that is, as long as any moisture remains, the temperature of the wool is very nearly that of the boiling point of water. If the wool remains in the dryer after water has evaporated, it then acquires the temperature of the dryer. If the temperature is high enough and the time of heating sufficiently prolonged, the wool may be yellowed. The change which causes yellowing apparently has only a small effect on the rate of dyeing. This is illustrated by dyeings with 3% Calcomine Fast Red 8B in a bath buffered at pH 4.2 as shown in Graph 5. In this case the yellowed wool samples had been heated for two hours and twenty minutes at 275° and 300°F. respectively.

EFFECT OF GREASE CONTENT

It is well known that the presence of moderate amounts of grease or spinning oils on wool will prevent it from taking up dyestuffs. For this reason better dyeing results will be obtained if the wool is properly scoured or the grease removed before dyeing. In Graph 6 dye exhaustion curves are shown for 3% dyeings of Calcomine Fast Red 8B at pH 4.2 on portions of the same batch of wool top containing various amounts of grease. The wool samples were prepared for dyeing in the following order:

(a) Original lot which contained 1.3% grease.
(b) Grease-free wool prepared by ether extraction of a portion of (a).
(c) Wool containing 1.2% grease replaced on a portion of (b) by treating with a lanolin—CCl_4 solution.
(d) Grease-free wool prepared by ether extraction of a proportion of (c).

The second ether extracted sample (d) was prepared to verify the fact that ether has no effect on the wool in causing a change in the rate of dyeing. This is confirmed by the fact that the two ether extracted samples dyed at practically the same rate; also the two samples containing 1.2 to 1.3% grease dyed at the same rate, but slower than the ether extracted samples.

EFFECT OF SCOURING

In the processing of new wool one of the first steps is the removal of dirt and grease. In place of the soap and soda scouring method, the solvent extraction method is frequently used. The difference in dyeing rate of wools "scoured" by these two methods is shown in Graph 7. Both wool samples were from the same lot of unprocessed virgin wool. Dyeings were made with 3% Calcomine Fast Red 8B at 95°C. in buffered dye baths at a pH of 4.2. If it is assumed that solvent extraction of wool causes little or no alteration in the wool fiber itself, it can be concluded that the faster rate of dyeing of the soap and soda scoured sample is due to some change in the wool closely related to "alkali damage."

NEUTRALIZATION

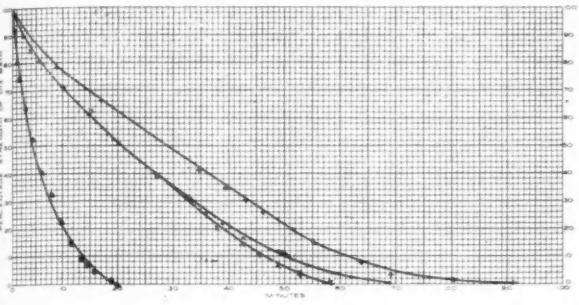
It is well known that the pH of the dye bath influences the rate at which dyes exhaust. The pH of the wool itself has been shown to have an effect upon the dyeing rate when it is entered into the dye bath[4]. In this study three samples of wool were pretreated in buffer solutions of pH's of 6, 5 and 4, respectively. They were dyed with 10% ammonium sulfate and 2% Calcocid Alizarine Green GG Extra, by starting at 100°F. and raising slowly to the boil. Graph 8 shows the dyeing rate curves for the three skeins. It can be seen that the greater the acidity of the skein being entered into the bath, the faster the dyeing rate. However, it should also be noted that all three came to the same equilibrium exhaust at the end of the dyeing. This would indicate that there was no major change in the wool due to the treatment by the various buffers but that the inherent acidity affected the rate of dyeing.

EFFECT OF CARBONIZATION

Non-uniformities in the carbonization of wool have been claimed to be the cause of unevenness in many wool dyeings. Some recent publications[5, 6] discuss this subject quite thoroughly and state that wool, carbonized with sulfuric acid, dyes lighter with acid dyestuffs than uncarbonized wool. In order to make quantitative dyeing rate measurements on carbonized wool samples, two wool skeins were given the standard AATCC carbonization with 5% sulfuric acid; one of the two skeins was neutralized with soda ash according to standard procedure and the other skein received no further treatment after removing from the oven. Both skeins were then dyed separately at 95°C with 3% Calcocid Alizarine Blue SAPG ex. conc. (C.I. 1054) in a bath buffered at pH 4.2. Graph 9 shows plots of percent dye bath strength against time for these two dyeings in comparison with a dyeing of an untreated wool skein. The difference in dyeing rate is only slightly beyond experimental error and is not as great as one might expect from statements in the literature. Another pair of carbonized wool skeins was dyed with Calcomine Fast Red 8B and the difference in dyeing rate was again insignificant. As a preliminary conclusion, therefore, it may be stated that at least in the case of two acid type dyestuffs mentioned here, sulfuric acid carbonization of wool does not cause a very significant change in the rate or extent of dyeing. A possible explanation for this discrepancy with statements in the literature is that the wool which was used may have been previously carbonized and further carbonization under the conditions stated produced no further change. Further investigation of this factor is being carried out.

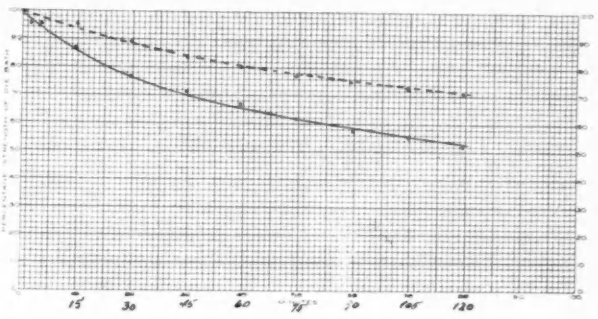
FULLING

Wool was given different fulling treatments and then dyed in the Dyeometer with Calcofast Orange 4R. The acid fulling treatment consisted of placing a 5 gram wool skein in a jar with steel balls together with 20 ml. of 0.3% sulfuric acid. The alkaline fulling bath consisted of 20 ml. of a solution prepared by adding 37.5 grams of sodium oleate and 15 grams of sodium carbonate to 1 liter of water. In carrying out the fulling operation the 5 gram skein was placed in a jar with steel balls and rotated for 2 hours in the Launder-Ometer at 90°F. When the samples were removed they were rinsed in cold water and allowed to stand in a pH 6 buffer solution for 48 hours. Just before dyeing, the skeins were boiled for 15 minutes in a pH 6 buffer solution. All dyeings were made using 2% Calcofast Orange 4R in a 80:1 bath buffered to a pH of 6.0. They were dyed at the boil for 90 minutes. Graph 10



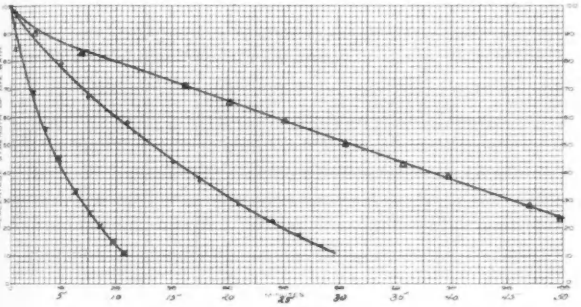
Graph 1

× *Sample No. 1.*
▲ *Sample No. 2.*
/ *Sample No. 3.*
· *Sample No. 4.*



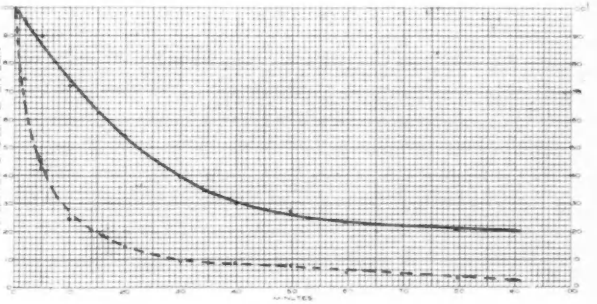
Graph 2

- - - - *B-3R Rugged* ———— *B-6 Unrugged.*



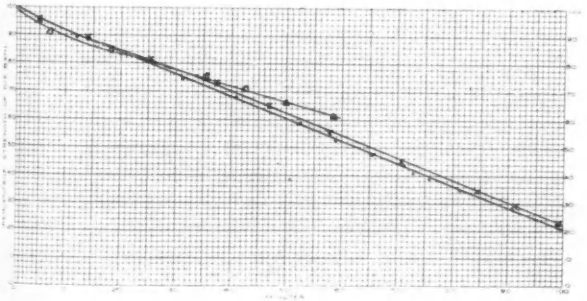
Graph 3.

Δ *Untreated wool.* · *Exposed to Fade-Ometer 130 hrs.*
× *Exposed to Fade-Ometer 280 hrs.*



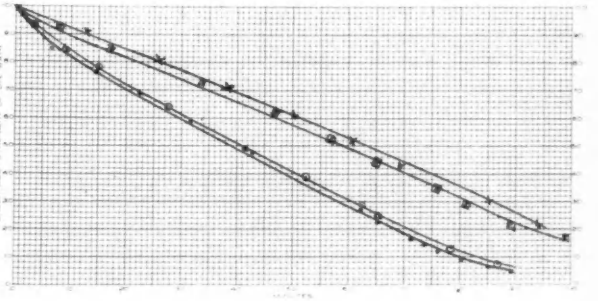
Graph 4

- - - - *Sliver—64's.* ———— *Sliver—36's.*



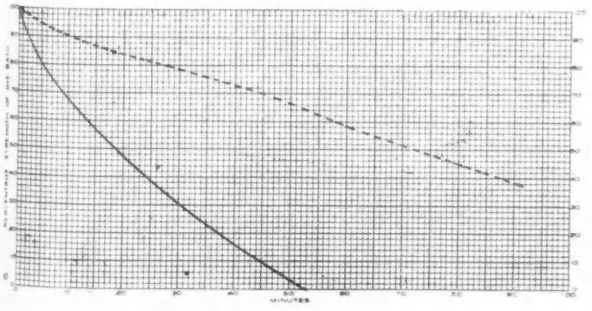
Graph 5

Δ *Unheated wool—control.*
· *Heated wool—2 hrs. 20 mins. @ 150° C.*
× *Heated wool—2 hrs. 20 mins. @ 136° C.*



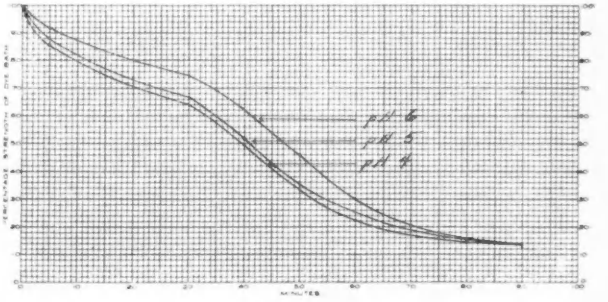
Graph 6

× *Skein before ether extraction, 1.3% grease.*
· *Skein ether extracted.*
⊠ *Skein after replacement of 1.2% grease.*
● *Skein after second ether extraction.*



Graph 7

———— *No. 1 soap and soda scoured (grease content 0.38%).*
- - - - *No. 1 gasoline extracted (grease content 0.39%).*



Graph 8

shows the curves for the dyeing rates of the acid and alkaline fulled wool and also for a control dyeing of the same wool which had been untreated. While the acid and alkaline fulled wool dyed slightly faster than the untreated wool, the difference is within the experimental error for the determination of dyeing rate. From this it can be concluded that with this particular dyestuff, fulling has little effect upon the dyeing rate if care is taken to bring the wool to the same pH.

EFFECT OF STOVING

(Sulfur Dioxide Bleaching)

Several wool samples were bleached by wetting out in distilled water and then placing in a large container through which sulfur dioxide gas was passed slowly for seven hours. After this treatment the skeins were washed thoroughly for over four hours in running distilled water. The rate of dyeing of one of these skeins with 2% Calcocid Phloxine 2G (C.I. 31) at 95°C. in a bath buffered at pH 4.2 is shown in Graph 11 in comparison with an untreated wool skein. It can be seen that the sulfur dioxide treated wool dyes considerably slower than untreated wool. Very little has been reported in the literature on the reaction of sulfur dioxide and wool, but it has been stated that sulfur dioxide treatment decreases the affinity for dyes by increasing the number of acid groups in the wool[6]. Probably the free amino groups (—NH_2) in wool are responsible for the affinity for acid dyes as indicated by the experiments of Elliott and Speakman[7] on acetylation and deamination treatments of wool as resist processes. It is, therefore, possible that sulfur dioxide forms coordination complexes with the amino groups thus reducing the salt forming capacity of wool; this concept of complex formation would agree with the fact that sulfur dioxide is not easily washed from wool. There are, of course, other reactions between wool and sulfur dioxide which bring about bleaching of the wool and which may further influence its affinity for dyestuffs.

EFFECT OF HYDROGEN PEROXIDE TREATMENT

In order to examine the dyeing rate of wool which has been bleached with hydrogen peroxide, several wool skeins were treated according to a procedure outlined by Townsend[6]. The skeins were treated at 40°C. and pH of 9.5 for three hours in 2 volume hydrogen peroxide. The rate of dyeing of such a treated wool skein is shown in Graph 11, the dyeing procedure being identical with that used in the stoving experiments. The result obtained agrees with the commonly accepted idea that hydrogen peroxide treatment decreases the affinity of wool for dyes. This is shown by the "equilibrium" exhaustion which in the case of the hydrogen peroxide-treated wool is about 82% as compared with over 90% for untreated wool. It should be noted, however, that the peroxide treated wool initially exhausts the bath at a much faster rate than the untreated wool so that if dyeings had been carried out for only ten minutes instead of fifty minutes or more the peroxide treated wool would have been considerably heavier than the untreated wool. One may conclude from these dyeing rate measurements that wool which has been treated with hydrogen peroxide probably has a decreased capacity for absorption of acid dyes but an increased reactivity which causes a more rapid absorption of dye.

EFFECT OF FORMALDEHYDE TREATMENT

As in the case of sulfur dioxide, formaldehyde might be expected to react with the free amino groups of wool and thus decrease the dyeing rate. That this is the case is shown in Graph 12 where the rate of dyeing of untreated wool is compared with that of formaldehyde treated wool. Dyeings were made at 95°C. with 2% Calcomine Fast Red 8B in a buffered bath at pH 4.2. The formaldehyde treatment of the wool skeins was carried out for one hour in a 4% formaldehyde solution at 70°C. These skeins were then wrung out without rinsing and air dried overnight.

It should be noted here that although formaldehyde reacts with the free amino groups of wool, it is also known to reduce the cystine disulfide groups at 70°C. and subsequently react with the thiol group thus formed[8, 9] which reactions may also have an effect on dyeing rate.

EFFECT OF DICHROMATE TREATMENT

An early method of bottom chroming wool was to boil the wool in an acidified potassium dichromate bath until the dichromate was reduced to the green chromic form all at the expense of oxidation of the wool. This method is not generally used now because it is recognized that severe oxidation of the wool and subsequent loss of tensile strength result from such treatment. In order to examine the effect of the dichromate oxidation of wool several skeins were boiled for one hour in a 0.067% potassium dichromate solution buffered at pH 4.2. They were then washed thoroughly in running distilled water but were still distinctly yellow from the color of the dichromate. Even repeated washings in both hot and cold water failed to remove the yellow coloration of these skeins. The rate of dyeing of this dichromate treated wool is compared with that of untreated wool in Graph 13. The dyeings were made with 3% Calcomine Fast Red 8B at 95° C. in a bath buffered at pH 4.2. The very slow rate of dyeing of the treated wool is probably due to a combination of various factors, the most important of which may be the presence of chromic compounds and excess dichromate in the wool.

CHROMIUM ACETATE PRETREATMENT

Race, Rowe and Speakman[10] have proposed the use of a specially prepared chromium acetate to rebuild various linkages in wool so as to obtain better fiber levelness. Wool was pretreated by this method. Graph 14 shows the dyeing rate curves for such specially treated wool and the same wool which had not been treated. The dyeings were made with 2% Calcocid Phloxine 2G at a temperature of 95°C. in a bath buffered to a pH of 4.2 with a bath ratio of 80:1. The data show that this pretreatment slows down considerably the rate of dyeing. Experiments with other acid dyestuffs gave a similar result. The microscopical examination of our dyeings shows poorer rather than improved fiber levelness by this treatment.

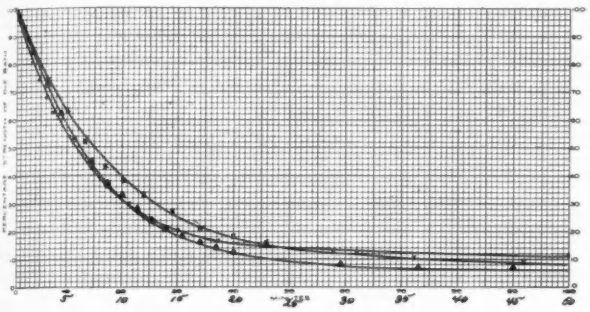
SULFOXYLATE TREATED WOOL

It is often necessary to strip dye from wool for redyeing purposes; this is frequently done with sulfoxylate. The curves shown here in Graph 15 for the untreated and sulfoxylate treated skeins are taken from a paper previously published by our laboratories[11]. The dyeings were made with 2% Calcocid Blue BL (C.I. 833) on the boil in an 80:1 dye bath at a pH of 6. It is evident from an examination of the dyeing rate curves that the sulfoxylate treated wool dyes more rapidly than the untreated wool. This seems to be a characteristic of acid dyestuffs on sulfoxylate treated wool.

CHEMICALLY MODIFIED WOOL

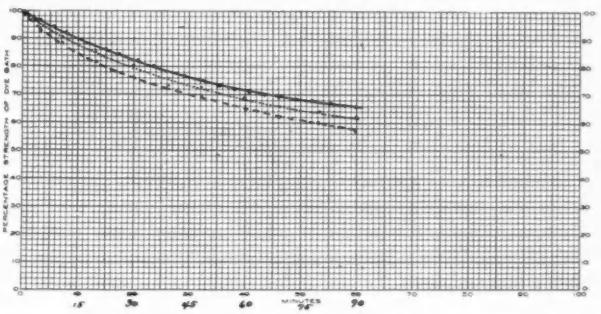
Harris and coworkers[12] have chemically modified wool by breaking down the cross linkages and rebuilding them with various other chemical constituents. Graph 16 shows the dyeing rate for such a chemically modified wool in comparison with the same wool untreated. The dyeings were made with 2% Calcofast Orange 4R in a dye bath of 10% sodium sulfate and 10% ammonium sulfate based on the weight of the wool. The dye bath ratio was 40:1 and the dyeing was carried out at the boil. 1% acetic acid was added after 30 minutes, 2% was added after 45 minutes and 1½% formic acid was added after 1 hour at the boil.

It is quite evident that the chemical modification of the wool changed the dyeing characteristics of the wool to a marked extent. Microscopical examination showed that the penetration of the dye into the wool fiber was more complete and the dyeing was more fiber level in the case of the chemically modified wool, see Figure 3, than with the untreated, see Figure 4.



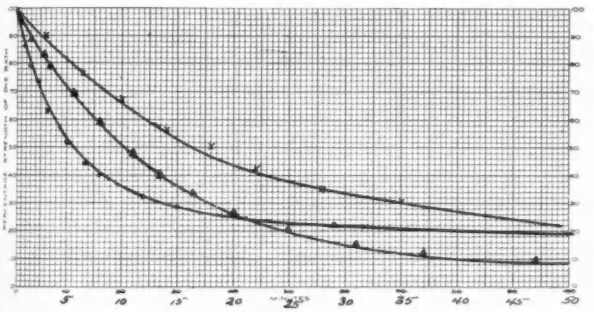
Graph 9

Δ *Untreated wool.*
· *H_2SO_4 carbonized—unneutralized.*
× *H_2SO_4 carbonized—neutralized.*



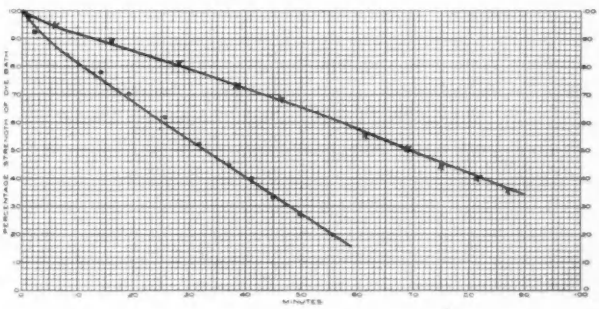
Graph 10

——— *Untreated wool.*
. . . . . *Acid-fulled wool.*
- - - - *Alkaline-fulled wool.*



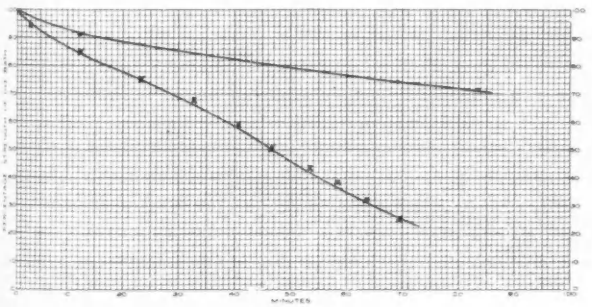
Graph 11

Δ *Untreated wool.*
· *H_2O_2 bleached wool.*
× *SO_2 bleached wool.*



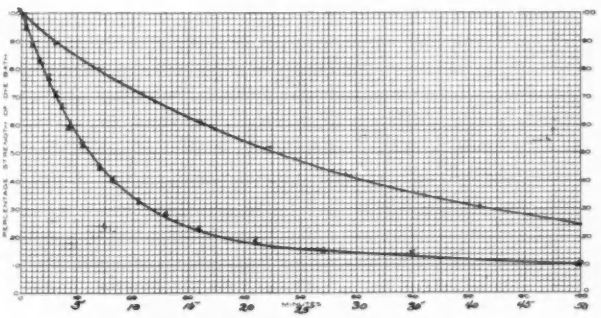
Graph 12

· *Untreated wool.*
× *Pretreated with formaldehyde.*



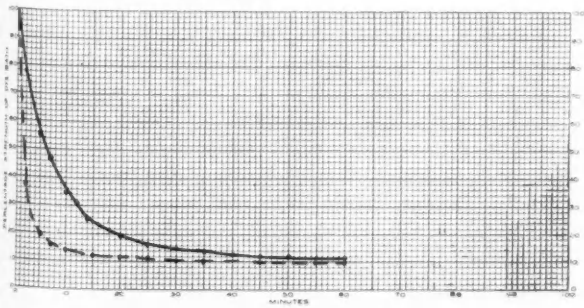
Graph 13

· *$K_2Cr_2O_7$ treated wool.*
× *Untreated wool.*



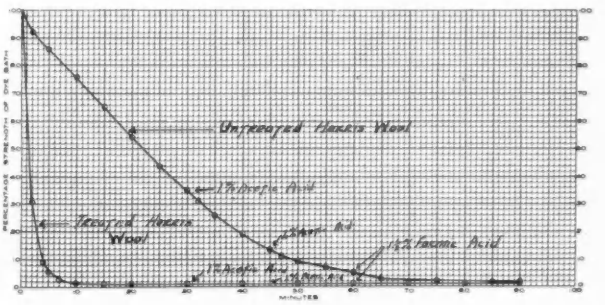
Graph 14

· *Pretreated with chromic acetate.*
× *Untreated wool skein.*



Graph 15

- - - - *Pretreated with sulfoxylate.*
——— *Untreated wool.*



Graph 16

PRETREATMENT WITH AN ANIONIC AGENT

In order to determine the effect of pretreatment of wool with an anionic agent, a 5 gram skein was boiled for 30 minutes in a 1% sulfuric acid and ½% Gardinol WA solution, the concentration of the sulfuric acid and the Gardinol being on the weight of the solution. The skein was then rinsed in cold water and allowed to stand for 48 hours in a pH 6 buffer. Before dyeing, the skein was boiled for 15 minutes in a pH 6 buffer solution. A skein of the same wool was treated in the same manner as above but the Gardinol WA was omitted. Graph 17 shows the dyeing rate curves for these two skeins, when they were dyed at the boil with 2% Calcofast Orange 4R at a bath ratio of 80:1 and a pH of 6. It is evident from the dyeing curves that the pretreatment with the anionic agent slowed down the rate of dyeing.

PRETREATMENT WITH CATIONIC AGENT

An article by Townsend[9] suggests the dyeing of wool in the presence of cationic active substances. In order to find out the effect of these substances, wool was pretreated with a cationic agent, the condensation product of ethylene oxide and octadecyl guanidine carbonate, and Graph 18 shows the effect of this pretreatment on the dyeing rate as contrasted to the dyeing rate of the same wool untreated. The dyeing was made with 2% Calcomine Fast Red 8B at the boil in a bath buffered at a pH of 4.2 with a bath ratio of 80:1. It is evident that the rate of dye absorption is very markedly increased due to the pretreatment with the cationic agent.

EFFECT OF BOILING IN WATER AND IN DILUTE AMMONIA

A wool skein was boiled for thirty minutes in a 0.004N NH_4OH solution. In Graph 19 the dyeing rate of this skein is compared with that of a skein which was boiled for thirty minutes in distilled water only and for further comparison the dyeing rate of an untreated skein is also included. Dyeings were made at 95°C. at a pH of 4.2 using 3% Calcomine Fast Red 8B. It is apparent that boiling in distilled water causes almost as much change in rate of dyeing as the boiling in dilute ammonia solution. It is suggested that this rather marked change in dye affinity of wool brought about by boiling in distilled water may be due to the absence of electrolytes in the water. This absence of electrolytes may facilitate the diffusion of products of hydrolysis from the wool as they are formed. Consequently the wool itself would be altered by such treatment and the affinity for dyestuffs changed.

EFFECT OF ALKALI

Much has been reported in the literature on the effect of alkali on wool and on proteins in general. It is well known that wool is degraded by treatment with alkaline solutions and one result of alkaline treatment is cleavage of the cystine disulfide links[13]. The effect of alkali on the tensile strength of wool depends on the concentration of alkali and the method of measurement (i.e. fibers or threads). With certain high concentrations of alkali there may be an apparent increase in tensile strength[11], but, in general, dilute alkali causes severe destruction of the wool. It appears to be common terminology to refer to this structural change in wool as "alkali damage"; but damage of this type should not be confused with other forms of so-called damage which may be totally unrelated to that caused by alkali. The increased affinity of slightly alkali damaged wool for dyes is, however, considered by some workers to be an advantage[15]. In order to measure quantitatively the effect of alkali damage on dyeing, several wool skeins were boiled for different lengths of time in dilute soda ash solutions. These skeins were then dyed at 95°C. with 3% Calcomine Fast Red 8B in a bath of pH 4.2. Two representative exhaustion curves are shown in Graph 20 in comparison with a curve for untreated wool. This plot shows that the more severe the alkali damage, the faster the wool takes up dye. This quantitative dyeing procedure is therefore a useful method of comparing the extent of alkali damage of wool samples providing these wools are identical in other respects. It has already been suggested[1] that measurements of rate of dye absorption is a more fundamental method of comparing variously damaged wools than the usually recommended staining techniques and the above experiments confirm this suggestion.

ALCOHOLIC POTASH TREATMENT

Freney and Lipson[16] have suggested an alcoholic potash method for the shrinkproofing of wool. In order to examine the effect of this method of treatment on dyeing, a 5 gm. wool skein was treated in 0.75% potassium hydroxide solution in 3A-alcohol for 30 minutes at a temperature of 20-24°C. The skein was wrung out and neutralized in a solution containing 5% sulfuric acid by volume. It was then washed with cold water until acid free and, before dyeing, was boiled for 30 minutes in a pH 6 buffer solution. The dyeing rate curves for an untreated skein and the alcoholic potash treated skein are shown in Graph 21. The dyestuff used was 2% Calcofast Orange 4R and the dyeing was carried out at the boil. After 30 minutes at the boil 1% acetic acid was added and, after 15 minutes longer, 2% more of acetic acid was added. At the end of 60 minutes boil, 1½% of formic acid was added.

The dyeing rate curves show very clearly that the alcoholic potash treated wool dyes much more rapidly than untreated wool. This has also been found with many other dyestuffs which have been similarly studied. Microscopical examinations show that good fiber level dyeings can be obtained on this type of wool with dyes which normally dye regular untreated wool with very poor fiber levelness. (See Figures 5 and 6 respectively.)

EFFECT OF HYPOCHLORITE TREATMENT

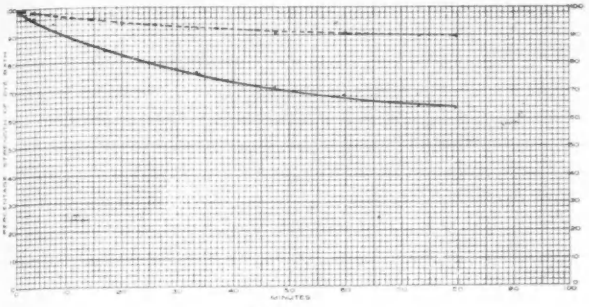
Chlorination and other closely related non-felting treatments for wool have varying effects on the affinity of wool for dyestuff. This must necessarily be true because of the wide variation in the reagents used for such treatments[17]. It is, however, commonly reported in the literature that chlorinated wool in general has a greater affinity for acid dyes and takes up these dyes at a greater rate [6, 17].

The dyeing experiments which are reported here were done on three wool samples which were kindly furnished by Smith and Harris of the Textile Foundation. One sample, designated as standard Hypol treated, was treated with 6¾% of 70% HTH (calcium hypochlorite)[18] and 2¼% of 70% pure p-toluenesulfonamide on the weight of the yarn over a period of 20 minutes and allowed to stand 10 minutes, then treated with 4½% sulfuric acid by adding the acid slowly over a 20-minute period, allowed to stand for 10 minutes, treated with 1% sodium bisulfite, rinsed and dried. A second sample was treated only by adding 6¾% of 70% HTH over a period of five minutes and allowing the mixture to stand for 25 minutes. One per cent of sodium bisulfite was added, and the yarn rinsed and dried. The third sample was untreated wool.

A comparison of the dyeing rates of these three skeins has been made with two different dyestuffs. Graph 22 shows the dyeings with 2% Calcocid Phloxine 2G (C.I. 31) at 95°C. in a bath buffered at pH 4.2. Graph 23 shows dyeings with 0.83% Calcozine Blue ZF (C.I. 922) at 80°C. in a bath buffered at pH 7.

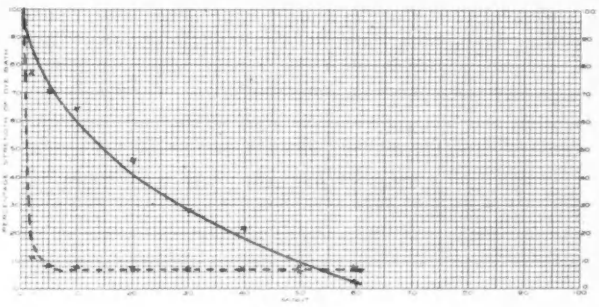
With Phloxine 2G, an acid dye, the standard Hypol treatment causes only a slight decrease in rate of dyeing while the sample treated with HTH only, dyed at a very much slower rate than the untreated sample. In the case of the Calcozine Blue ZF, a basic dye, both of the treated samples dyed at the same rate but faster than the untreated sample. The results with the acid dye are in definite disagreement with the literature.

Further information was obtained by making microscopical examinations of



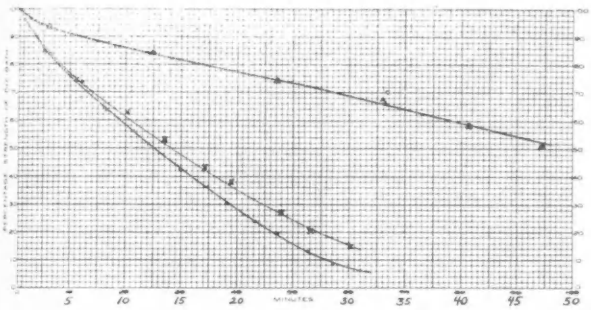
Graph 17

- - - - *Pretreated with Gardinol WA + H_2SO_4.*
———— *Pretreated with H_2SO_4.*



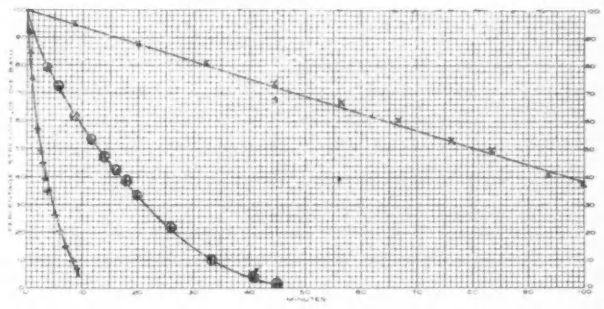
Graph 18

- - - - *Pretreated with cationic agent.*
———— *Untreated wool.*



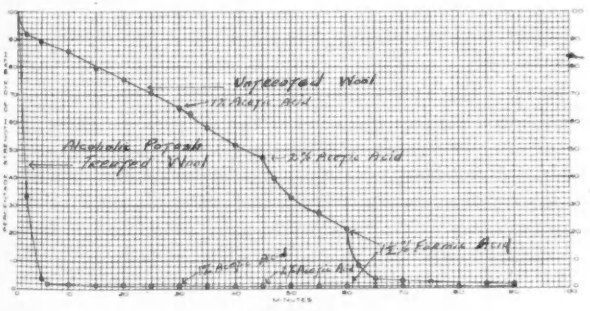
Graph 19

· *Wool preboiled ½ hr. in 0.004 M NH_4OH.*
× *Wool preboiled ½ hr. in distilled water.*
Δ *Untreated wool.*

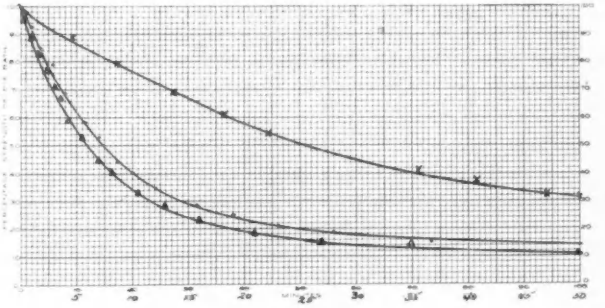


Graph 20

× *Untreated wool.*
Moderately damaged in Na_2CO_3 solution.
\+ *Severely damaged in Na_2CO_3 solution.*

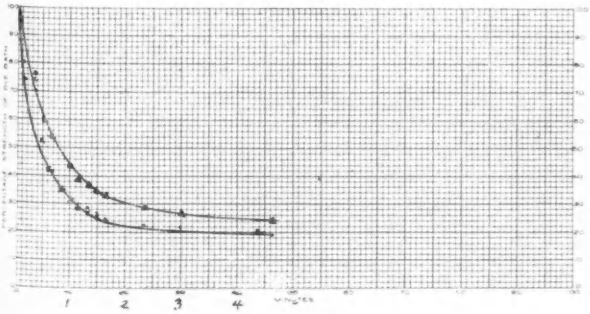


Graph 21



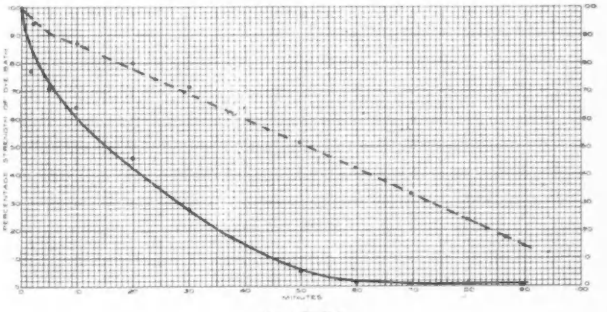
Graph 22

Δ *Untreated skein.*
· *Standard Hypol treatment.*
× *Pretreated with hypochloric only.*



Graph 23

Δ *Untreated wool.*
· *Standard Hypol treated wool.*
× *Calcium hypochlorite treated.*



Graph 24

- - - - *Pretreated with M-3.*
———— *Untreated wool.*

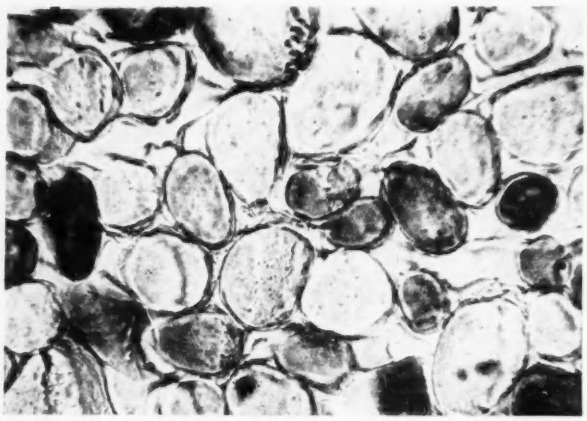


Figure 1

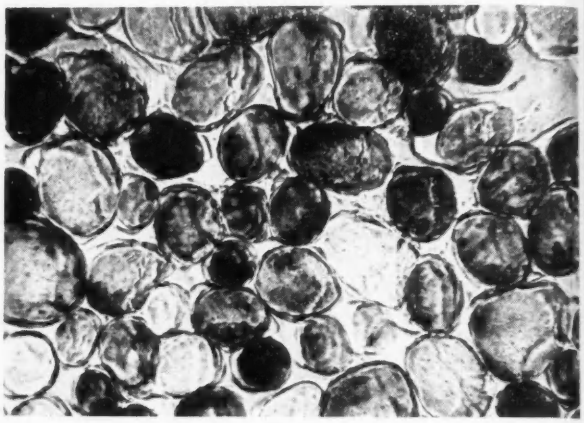


Figure 2

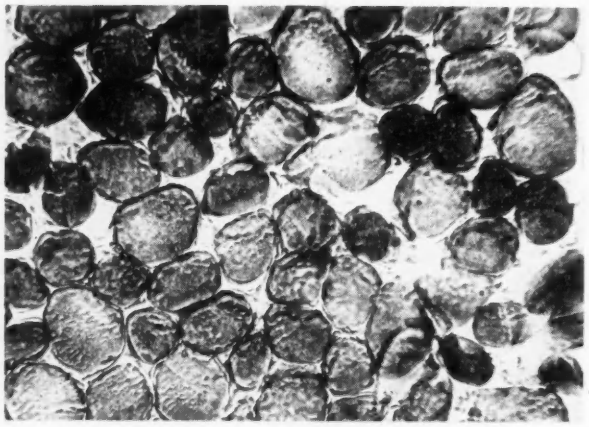


Figure 3

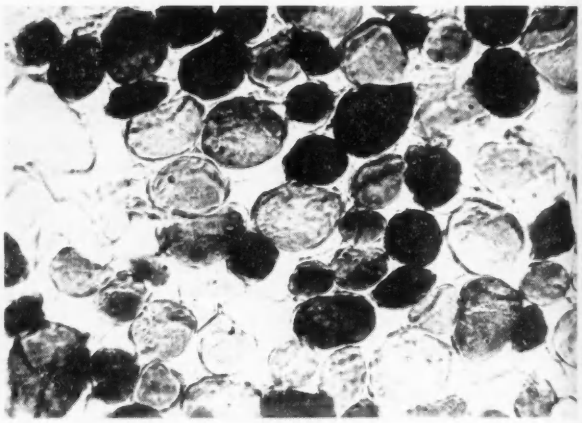


Figure 4

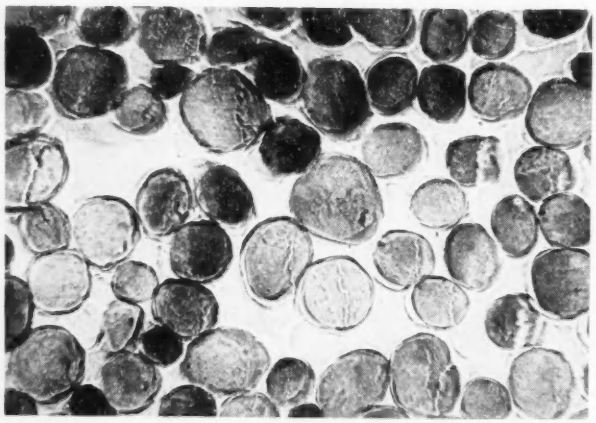


Figure 5

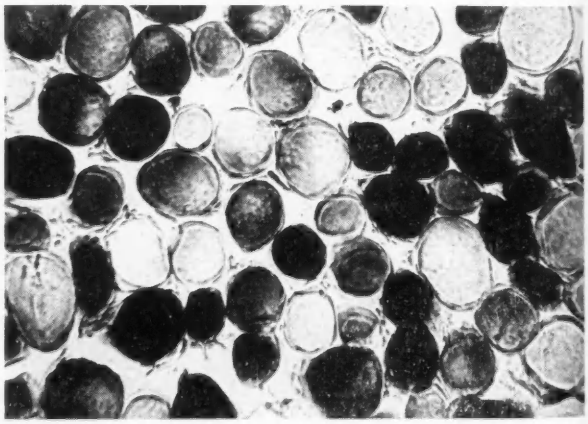


Figure 6

cross sections of the untreated and Hypol treated dyeings. Figures 7 and 8 show the Hypol and untreated dyeings, respectively, dyed with Calcocid Phloxine 2G. While it is difficult to see, the outside of the Hypol treated fibers are undyed and inside dyed. The untreated fibers are dyed throughout. In Figures 9 and 10 the dyeings for Calcozine Blue ZF are shown. The Hypol treated, Figure 9, is dyed very strongly on the outside of the fibers and very lightly inside. The untreated fibers, Figure 10, are only lightly dyed except for a few "damaged" fibers which dye heavily. The "ring" dyeing of chlorine treated wool with a basic dye, Phenosafranine, has been reported previously[17].

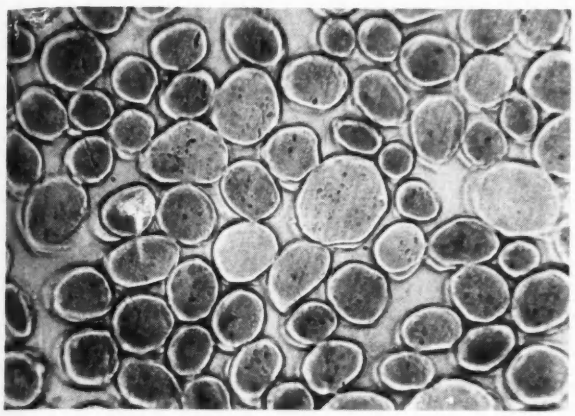


Figure 7

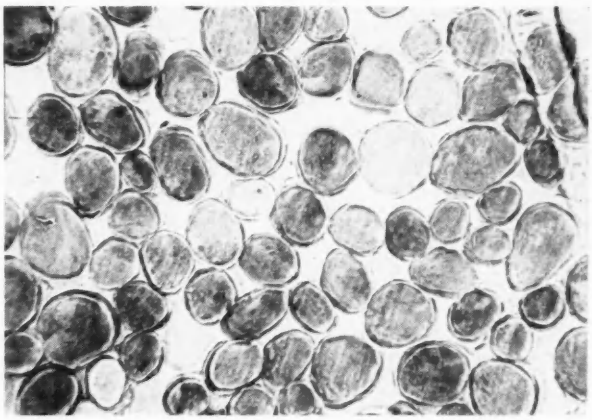


Figure 8

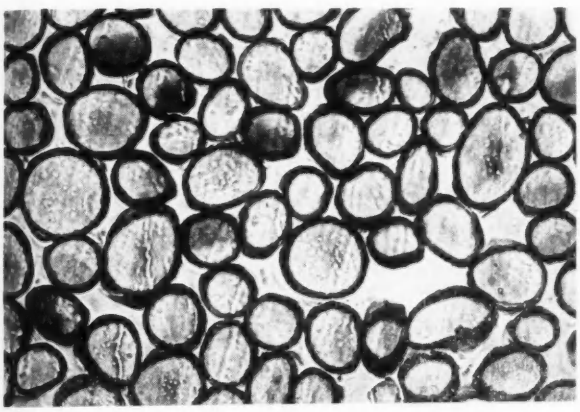


Figure 9

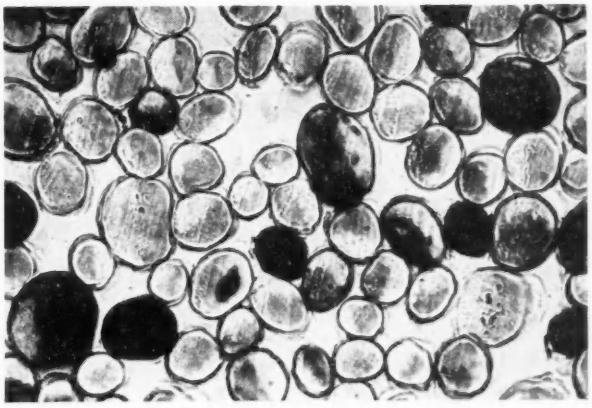


Figure 10

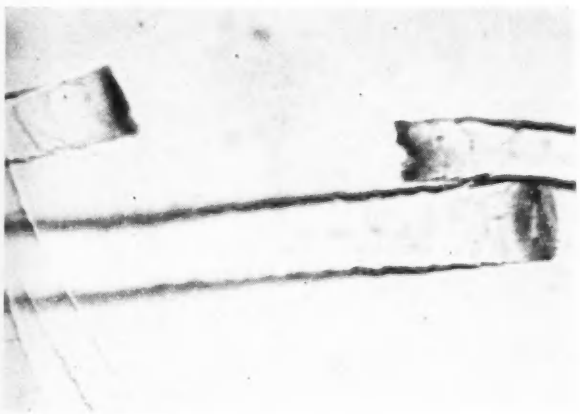


Figure 11

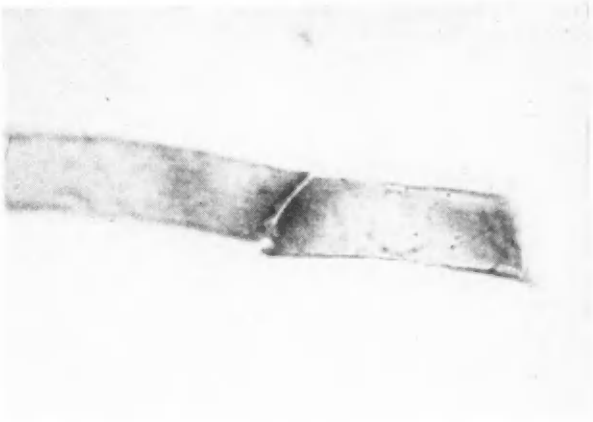


Figure 12

No further discussion of the above results can be made at the present time, since the dyeing of this type of treated wool is still under investigation.

RESIN TREATED WOOL

Wool which has been treated by the Lanaset (Trade Mark of Calco Chemical Division, American Cyanamid Company, applied to a melamine resin of its manufacture for use in wool shrinkage control) process dyes much slower than the same wool untreated. Graph 24 shows the dyeing rate curves for a treated and untreated skein dyed with 2% of Calcomine Fast Red 8B in a bath buffered at a pH of 4.2. Dyeing was carried out at the boil in an 80:1 bath.

Microscopical work which has been

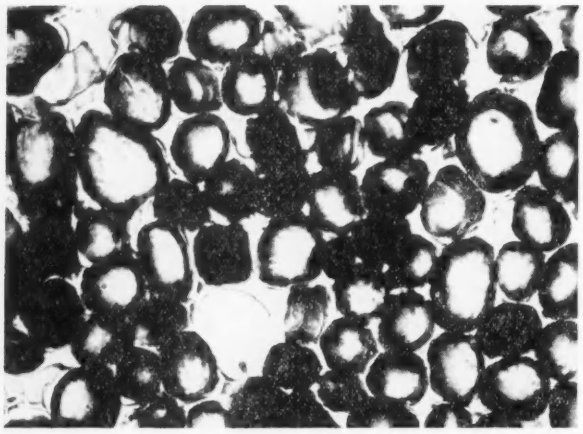


Figure 13

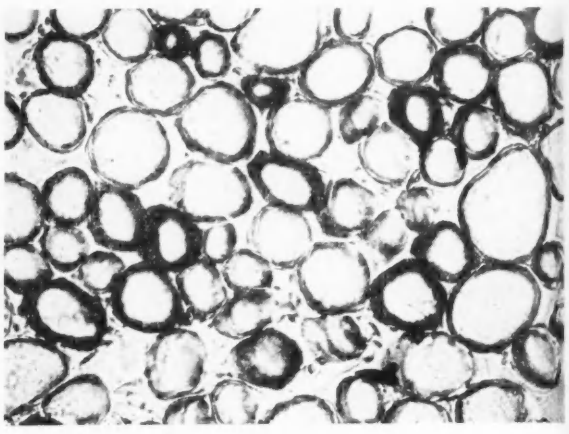


Figure 14

done indicates that the resin is deposited largely within the wool fiber itself. Figures 11 and 12 show dyeings made under the microscope with Calcocid Blue VS (C.I. 712) on treated and untreated wool respectively. These wool fibers were cut before dyeing so as to expose freshly cut ends to the dye solution. This permitted the dye solution to come into direct contact with the center of the fiber which had not previously been in direct contact with the resin solution. It can clearly be seen that the dye readily penetrated into the cut ends of the untreated fibers but it does not penetrate rapidly into the ends of the treated fibers. From this, it is concluded that the resin has penetrated into the center of the fibers and thus prevented the dye from diffusing rapidly into the freshly cut ends. Cross sections have also been made of treated and untreated wool which had been dyed with Calcozine Blue ZF before sectioning. Figure 13 for untreated wool and Figure 14 for treated wool show that the dye has penetrated farther into the untreated fibers than into the treated fibers for the same time of dyeing. It can, therefore, be concluded that the resin treatment of the wool slows down the rate of dyeing and thus very markedly affects the dyeing properties.

SUMMARY

In conclusion it may be stated that according to the results of this investigation those factors which cause an increase in the rate of absorption of acid dyes by wool are: natural weathering, light exposure, hydrogen peroxide treatment, sulfoxylate treatment, chemical modification, treatment with cationic active agents, boiling water treatment and treatments with alkaline solutions. The following factors cause a decrease in the rate of absorption of acid dyes by wool: the presence of oils or grease, treatments with hypochlorite, formaldehyde, bichromate, chromic acetate or anionic active agents and resin treatment used for shrinkage control. The pH of the fiber, method of scouring and the fiber size also have an influence on the dyeing rate, while fulling, carbonization and oven drying were found to have little or no effect. Although hydrogen peroxide treatment is listed above as increasing the rate of absorption of acid dyes, such treatment decreases the extent of final exhaustion.

It is hoped that the gathering together of these many factors which cause variations in the dyeing properties of wool, may be of assistance in clarifying the many practical problems which face both the colorist and the dyer.

ACKNOWLEDGMENT

The authors wish to acknowledge the help received from their associates in the Research Department and Microscopical Laboratory of the Calco Chemical Division, American Cyanamid Company, in securing data and preparing this paper.

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DISCUSSION

Chairman Harris: Thank you, Dr. Kienle.

Mr. Christison of the Arlington Mills will offer a few comments on the paper.

Hugh Christison: Dr. Kienle has certainly given us a very good paper, and he has emphasized what the wool man has been up against since the beginning, and that is, there is very little he can do to the wool without modifying its dyeing properties. The paper somewhat surprised me because either Dr. Kienle is mistaken or some of us mill men know a lot of things that are not so.

For instance, in the case of sulfur dioxide and sulfuring, we always felt, and in practice thought, we would make use of the fact that we could increase the affinity of wool for dyestuffs by sulfuring. For a good many years some of the mills would sulfur their wool for the sole purpose of increasing the affinity of the wool for dye, particularly in vigoreaux printing.

Then, to see evidence that the rate was decreased was a little bit disconcerting.

Of course, there is another point. I think that most of this work was done where the samples were dyed not together but separately, and when that is done, it rather changes the picture, for it complicates the rate and the amount of dye absorbed. The wool man, I think, is troubled more by the various amounts of dye that absorb rather than the rate. For instance, in carbonizing, we have always believed that carbonizing would usually suppress the capacity of the wool to dye, and the impression that we gather here is that the carbonizing has not caused very much effect. However, we do know, from practice, that the carbonizing effects are usually toward the suppression of the wool capacity to absorb dye, and we always get lighter spots or streaks in carbonizing

defects rather than darker.

As regards the weather and the light, that is quite important to mill men, because that comes back to the question of tippy wool. A few years ago Von Bergen did some very interesting work on that. He found that you could divide the dyes into two classes. He called them, for want of a better term, negative and positive. He found that with some of the dyes, for instance, a typical color like Alizarine Blue SAP, made little difference whether the wool was exposed to light or not, and yet some of the other dyes dyed more strongly on the tips or light struck places and some dyed more strongly on the butts.

I don't think that you can make a general statement that the light does affect wool one way or the other. We do know that it does affect the wool, and all of us have seen plenty of defects that have been so caused.

There are some things that weren't mentioned here. Two of the most conspicuous ones that bother the wool men are steam and mildew. They are very practical problems, and we run up against them every day. At the present time, steaming is quite important because we have to set our yarn. Our yarn goes through so fast that we haven't time to let it stand and reach equilibrium, so we resort to steaming to set it. Steaming causes all sorts of complications if it isn't done evenly. The tendency of steam, as a whole, is to rather markedly increase the affinity of wool for dyes.

Mildew is a thing that the mill man also is continuously up against, especially in a season like the last. Again, like light, sometimes mildew causes an increase of affinity for the dye and sometimes a decrease. I think that most of the tendency is to cause a so-called resist spot.

Tannic acid wasn't mentioned. Sometimes the mill men make use of that to what you might call resist the tendency of the wool to take up dye.

There is another point the speaker made about synthetic resins, the idea being that the evidence is that the resins have penetrated the fiber. Personally, I rather question that. I think the effect he got probably was from the effect of formaldehyde rather than the effect of the resin. Of course, he stated in his paper that the effect of formaldehyde was to depress the affinity of the wool for dye. As far as I know, one of the conspicuous indications you get when using the synthetic resin is the liberation of formaldehyde. Is that so?

Dr. Kienle: That is right.

Mr. Christison: I think it is probably the formaldehyde effect rather than the resin effect that you are getting with your wool.

As regards sulfoxylate, your results check with ours, but there is one thing that we should all keep in mind there, and that is that it is quite important that the sulfoxylate be destroyed because a good many times, unless you are careful, the wool retains sulfoxylate, and you get the effect of the sulfoxylate itself on the dye rather than the effect of the wool that has been modified.

However, the paper certainly has given us a lot to think about, and I think it is quite valuable. (Applause)

Chairman Harris: As everyone here knows, the real tendency in the textile industry has been a continuous rather than batch processing. There has been a marked increase in the number of mills that are now doing continuous bleaching, for example, of cotton, and just recently continuous dyeing has come into use through the efforts of various concerns. I think we are very fortunate to have Werner Von Bergen, who has been one of the pioneers in this field, agree to present a paper. He is going to discuss "Continuous Indigo Dyeing of Wool Stock."

. . . Mr. Von Bergen presented his paper. (Applause)

CONTINUOUS INDIGO DYEING OF WOOL STOCK*

W. VON BERGEN, T. CROWLEY and W. BROMMELSIEK

Presented by Werner von Bergen

ON December 4, 1942, George Linberg of the Du Pont Company reported to the New York section of this association about the first successful continuous indigo dyeing on woolen piece goods.

It is my privilege today to report to you a further achievement in this same field of continuous dyeing of animal fibers, namely, the continuous indigo dyeing of wool stock.

As in the case of the continuous piece dyeing with indigo where the success of a research development was made practically applicable through the combined efforts of the technical staffs of both the Hampshire Woolen Mills and the Du Pont Company so it was with the continuous stock dyeing where the coordination of minds of both the Forstmann Woolen Company and the Du Pont Company led to a successful installation.

The Hampshire Woolen Company method was excellent for dyeing the 11 oz. flannel, but difficulties were encountered with heavier goods. To overcome this difficulty Linberg stated that the Du Pont Company had developed a method of padding a sufficient quantity of indigo on to completely fulled meltons, representing the same amount of indigo bottom as one would ordinarily apply on top of an alizarine bottom in stock dyes. After the padding the goods are given a slight scouring and are then dyed with an appropriate formula of chrome colors to produce the Navy shades. The application of the same process on Kerseys is still under investigation.

The process and the adoption of these new methods by the woolen mills was very slow, far too slow for the ever increasing demand of the Navy. The table below reflects clearly this tremendous increase in the Navy demand for woolen cloth.

TABLE I

Estimated Deliveries of Principal Cloths for the Navy (including Coast Guard)*
(In thousands of linear yards)

Item	Purchases January 1, 1940, to January 1, 1944	Estimated Deliveries in:			
	1940	1941	1942	1943	1944
30 oz. Kersey	550	526	2,183	4,800	1,259
16 oz. Melton	755	1,280	6,509	14,200	10,056
11 oz. Flannel	268	1,463	3,811	8,200	2,247
Total Navy and Coast Guard	1,573	3,269	12,503	27,200	13,562

* Source Bulletin National Assn. of Wool Manufacturers, 1943.

At the outset of the war, relatively few manufacturers were equipped to produce large quantities of indigo dyed material. New manufacturers hesitated and were reluctant to take up methods which involved various operational difficulties such as outmoded, sloppy and dirty hand labor in its application and the smearing created in the other manufacturing processes. The Navy in order to fill its quota was obliged to relent in its requirements by granting the mills permission to fulfill their contracts with the leuco ester of indigo combined with chrome dyes or with 100 per cent chrome dyed material. However, this relaxation of the color specification was neither a boom to the manufacturer nor to the Navy. The difficulties encountered in dyeing with 100 per cent chrome colors was innumerable, with the result that the Navy was obliged to accept an inadequate

* Presented at Annual Meeting, Atlantic City, N. J., October 14, 1944.

substitute for indigo with regards to shade and fastness properties.

Furthermore, considerable difficulty was encountered in meeting Naval specifications for fabric breaking strength even so in case of the melton the Navy had lowered the specification about 10 per cent. General dissatisfaction with the entire dyeing results led to the abandonment of the chrome-dyed deliveries and the insistance of the Navy upon the indigo shade.

The Navy was willing to accept as only alternative the application of leuco esters of indigo in conjunction with chrome colors. A compromise method, as pioneered by the Du Pont Company for the 16 oz. Melton, using a two bath process was finally adopted by several large mills. The process is a combination of continuous piece dyeing and kettle dyeing. The pieces are first run through a tank similar to the one used in piece carbonizing then after oxidizing and washing topped with chrome colors in regular piece dye kettles. Other mills adopted the method proposed by the General Dyestuff Corporation, using a combination of Algosol blue and chrome colors in straight piece dyeing, as reported by Derby. These two methods gave the Navy an ample supply of melton, but still could not satisfy the demand for the 30 oz. Kersey, where piece dyeing was out of the question. Although the appearance and fastness of the indigo shade were simulated through this dyeing procedure, the same operational disadvantages encountered in using the chrome colors were found to exist. The excessively prolonged dyeing time, due to the complexity of the chemical nature of this process resulted in difficulty in meeting yarn and fabric specification for breaking strength. Moreover, the considerable increase in the dyeing time prevented meeting of production quotas, not to mention the much higher dyestuff and labor cost involved.

In the fall of 1942 William Wentz of the Du Pont Company approached The Forstmann Woolen Co. with the idea of continuous stock dyeing. Samples were made on a laboratory wool scouring machine and they proved the workability of this idea. In the spring of 1943, in view of the unsuitability of the various substitutes as manifested by the numerous trials, the decision was made to build a continuous stock dyeing machine for the attainment of the full indigo shade.

In close cooperation with the technical staff of the Du Pont Company, especially with Mr. Wentz, the originator of the idea, preliminary trials were conducted. The indigo dyeing was carried out continuously, utilizing the final two rinse bowls of a Hunter wool scouring train. One vessel served as a dye vat in which the material was accorded a one minute immersion or dip, the excess vat liquor was squeezed out and the dyed wool subjected to a one minute immersion in an oxidation bath which chemically reconverted the indigo from the leuco to the insoluble state. The material was then transported to the dyehouse and topped with chrome colors in such quantities as to attain the desired shade. The improvement effected by this change in dyeing technique was most encouraging as regards the breaking characteristics of the yarn and the finished cloth. However, the shade achieved was as yet not in accord with Navy demands; evidently, the reversal of the specified dyeing application which indicated indigo dyed material with a chrome bottom, resulted in a predominance of the chrome colors with a concealment of the typical indigo shade characteristics.

The Navy was very cooperative in accepting the trial shade and for three months until the completion of the new machine, we very successfully combined wool scouring and indigo dyeing in one process.

With this brief historical description of the events from which evolved the continuous indigo stock dyeing, the exposition of the chemical and the mechanical phase of the process may be undertaken.

Werner von Bergen is Director of Research and Control Laboratories of the Forstmann Woolen Company, Passaic, N. J. A native of Switzerland, he graduated as a chemist from Technical College, Burgdorf, Switzerland, in 1916. His experience in woolen manufacturing dates back to 1919. For one year he was connected with I. G. Farbwerke, Leverkusen, Germany, and has been with Forstmann since 1926. Mr. von Bergen is an authority on the processing of wool with many publications to his credit. He is co-author of the American Wool Handbook and the Textile Fiber Atlas. He conducts a course on woolen and worsted manufacture at Columbia University. He is chairman of A3, Section I on Wool of the American Society for Testing Materials and is an associate member of the Textile Institute.

CHEMICAL PHASE

For continuous stock dyeing the hydrosulfite vat which is free from sediment is the only one suitable. The depth of shade obtained is a function of four variables, the number of dips, the proper oxidation, the immersion time for each dip and the concentration of dyestuff and chemical auxiliaries in the vat. *Caustic soda* serves as the alkaline provider which regulates the solubility of the indigo. The reduction of the indigo to its leuco state is accomplished through the use of *hydrosulfite*. The oxidation products of the reducing compound formed within the liquor are governed by a buffer action set up by *soda ash* which is another component of the bath in conjunction with caustic soda. The alkali concentration must be carefully maintained at prescribed limits so as not to produce a pH exceeding the point where the wool fiber may be damaged. Furthermore, the concentration must be sufficient to assure the solubilization of the indigo. It has been established that indigo white will not be precipitated from solution in the presence of *ammonia* and *glue*. Ammonia alone is incapable of achieving this result; however, in the presence of glue, the indigo white may be retained in suspension.

The second phase of the continuous dyeing process is the re-transformation of the indigo white back to the insoluble state with its fixation within the fiber. It entails an oxidation of the hydroxyl groups to the original keto radicals within the indigo molecules. The oxidation process is negotiated by auto-oxidation, i.e., by the action of atmospheric oxygen, of the dyed stock from which the excess vat liquor has been squeezed and by the utilization of chemical oxidation compounds in which case the oxidative process is greatly accelerated.

As mentioned previously, the depth of shade evolved may be adjusted by the number of dips to which the material is subjected. Naturally, the color absorbed within the fibers must be oxidized or fixed after each immersion before the material is given another dip.

In continuous stock dyeing, in order to dye the full indigo shade, two dips are necessary. Likewise, two oxidation steps must be included.

This process, wherein the material is dyed continuously on a productive scale, demands that the oxidative processes carried out after each dip, must accomplish their functions in a short space of time, especially after the first dip. The chemical agents utilized for this purpose, generally are concentrated *hydrogen peroxide* solution and *sodium perborate*.

In addition to the two main phases discussed, certain facilities are provided which satisfy specific functions, namely, wetting and rinsing. Prior to the first indigo dip the wool must first be tho-

roughly wetted out, so as to avoid the introduction of air imprisoned between the wool fibers. The detrimental effect of the presence of free oxygen in the vat liquor cannot be over-emphasized. After the oxidation which the material undergoes after the first dip, the excess oxidizing agent must be rinsed off in order to avoid its carry-over into the second dye vat. After the second oxidation bath, the wool must be thoroughly rinsed in order to remove the superfluous color as might be adhering to the surface of the fibers and which would result in excessive smearing in the subsequent mechanical manufacturing operations.

MECHANICAL ASPECTS

With this brief synopsis of the continuous indigo dyeing process, the next consideration will be to examine structural and mechanical aspects of the machinery utilized for its functioning. The dye train with an overall length of approximately 200 feet is more or less a duplicate of a raw wool scouring train. It consists of eight bowls or stationary vats, interconnected by squeeze rollers and mobile aprons in which the wool is transported through the bowl liquors at a fixed rate of speed by the propelling motion of harrow forks (see figure 1). To synchronize the movement of the wool stock through these various types of vessels with the proper liquor circulation and feed, followed by the drying operation, a total of 60 motors of various sizes and types are utilized.

Each bowl in the dye train performs a specific function. The first bowl serves to wet out the scoured wool prior to its entrance into the dye vat; the second and sixth bowls constitute the dye vats; and the third and fifth bowls act as the oxidation baths; and the fourth, seventh and eighth bowls perform a rinsing operation. As regard dimensions, mechanical and structural operation, the two dye vats are larger and slightly different from the others. Basically, the construction of all eight bowls are similar. Each bowl is divided horizontally into two sections by a perforated iron plate, which extends along its entire length, approximately one foot below the top rim of the bowl.

Temperature equilibrium is maintained throughout operation by thermostatically controlled heating coils, also located in the segment of the bowls directly below the perforated plates. Regular steam inlets are incorporated in each bowl for adjusting the liquor temperature to the desired level in the shortest time when starting up with fresh liquors. The squeeze rollers located at the extremity of each bowl direct the excess liquors into an overflow compartment, separate from the bowl proper, from which the liquor may be pumped back as the beginning of each bowl in the case of the wetting out and the oxidizing and rinsing baths or pumped to other points in the circulatory system as in the case of the dye vats.

The feeding mechanism utilized in introducing the wool to the first bowl is a feed hopper. The wool is transferred from the feed box into the bowl proper by means of a spiked table. The delivery is regulated so as to assure even feeding and to maintain a production of 550 pounds of scoured wool per hour. The material is fed manually from the open bale into the feed hopper. The wool is fed into the three succeeding bowls by means of a traveling table or apron which gathers the wool as it emerges from the rollers and deposits it into the following vessel. However, after the first rinse bowl, prior to the second dip, the wool is dropped into a second feed hopper. This operation permits a certain degree of opening of the wool so as to facilitate adequate penetration of the liquor into the material in the second dip. After this dip, the wool is squeezed and dropped into a conveyor belt and transported to another feed hopper which proceeds the second oxidation bath. This mechanism is necessary because of the dyeing train being extended over two rooms in the dye-house and a conveyer serves as the connecting link between the two separate parts of the unit. During its transportation along the conveyor and during its period of standing in the feed hopper, the material undergoes a certain amount of air oxidation which has its effect upon the chemical requirements of the second oxidation dip. The material is introduced into each of the other three bowls which follow by means of mobile aprons after the squeeze rollers. The wool from the last rinse bowl is transported from the moving lattice into the feeder preceding the drying oven.

The propelling motions which govern the transportation of the wool through the dye train differs slightly for the dye bowls as compared with the others.

However, the essential elements of the movements which are accomplished by the use of harrow forks are similar. They consist of series of parallel rakes, each containing a similar number of prongs and operated on an off-center cam which governs the distance of the fork sweeps. The period of each sweep is gear-controlled and powered by a single separate motor. The immersion time required for the various baths are regulated by different sized gears which govern the frequency of the individual harrow fork sweeps. The motion of the forks is such as to propel the material through the liquors gently and with a minimum of agitation. This is mandatory in the dye vats where agitation would result in the introduction of oxygen with a resultant precipitation of the indigo blue. In the dye bowls, before the wool reaches the range of the harrow forks, as it is dropped from the moving aprons which conveys it from the squeeze roller, it is submerged completely into the dye liquor by action of a ducker. This mechanism is a wooden rotating cylinder, equal in length to the width of the bowl, which sweeps the bowl beneath the surface of the liquor by the action of transverse blades. The thorough immersion of the material is essential to obtain even penetration of the vat liquor into the clumps of fibers. The rotation of this ducker is controlled by a separate motor. On the other bowls, the wool is swept into the range of the harrow forks by the force of a spray of the squeeze liquors.

The delivery device carries the material along the incline at the end of each bowl and presents it to the squeeze rollers. On the dye bowls, this lift must operate rapidly so as not to allow the material to stand partially exposed in the air before the excess liquor is squeezed out. For this reason, a separate slide lift, a crab, is utilized which is powered by the same motor drive governing the movement of narrow forks, but which is geared to a higher speed. The crab itself is comprised of several rows of metal prongs of ever increasing length operating over a certain area within the bowl. The delivery mechanism of the other bowls is merely an extension of the narrow fork tilted at a slight angle and containing shorter length prongs in order to transverse the incline of the perforated bowl bottom at the end of the bowl.

The squeezing of the excess liquors from the material, so important to efficient operation of the vat liquors, is affected by two heavy rollers, in contact under a certain compression and rotating under a fixed rate of speed. The top roller, which is slightly larger in diameter, is lapped with hard rubber, while the bottom roller is constructed of iron. The speed of the rollers is controlled by gears and the rollers of each machine are driven by a separate motor. The speed of rotation of the rollers on the dye bowls is approximately twice as high as on the other bowls. They are built right in the bowls with the bottom roller nearly immersed in the dye bath, in order to squeeze the excess liquor from the material before it has an opportunity to absorb atmospheric oxygen. The squeeze liquor from these bowls is passed into a compartment from which it is pumped to the second dye vat or to the regeneration tank. Naturally, the extent

of the oxidation in the squeeze liquors determine the chemical requirements of this regeneration process.

After the final rinse, the material is deposited into a feed hopper from which it is transported into the dryer along a spiked table. The wool is then dropped into a continuous lattice which travels the length of the dryer. It emerges finally at the opposite end of the dryer where it is bagged for transportation to the wool spinning mill. The speed of the dryer is such as to dry the production capacity of the dyeing train to the required moisture content of approximately 10 per cent. It takes the wool 45 minutes to travel from the first feeder of the machine to the outlet of the dryer. The machine was built by the C. A. Sargents Sons Corporation according to blueprints from the Forstmann Woolen Company, Engineering Department.

DYE LIQUOR CIRCULATING SYSTEM

Aside from the train itself, the dyeing system also includes provision for circulation and replenishment of the liquors and facilitates the preparation and distribution of stock solutions of color and chemicals required for the consummation of the dyeing process. The dyestuffs and auxiliary requirements are weighed and mixed in accordance with the mixing procedure and the dye recipe. The introduction of the color into the dyeing machine proper is maintained by a circulatory piping system which permits the solutions to be directed into the first and second dye vats or dispersed equally between the two. The overflow and squeeze liquors are then pumped back into the feed tank for regeneration and replenishment of the color absorbed by the material. At this point we must state that the success of this or any other continuous dyeing is entirely dependent on the synchronized flow of both, the material to be dyed and the dye liquor through the machine. Any fluctuation in the flow of one or the other components is a direct cause for the failure of the bath. As the material flow is regulated mechanically, no great variation should occur, but the liquor flow procedure must be developed to meet the demands. For the accomplishments of this purpose, four tanks are utilized, one of which has a 400 gallon capacity and three others a 1,000 gallon capacity. The tanks are all inter-connected and provided with pumping facilities, so that the solutions may be passed from any one tank into another. Each tank is equipped with hot and cold water inlets as well as with an internal steam coil system, thermostatically controlled in order to maintain the correct vat liquor temperatures. In Figure I may be seen a flow diagram of the circulatory system. The slurry tank is equipped with a large stirrer, required for slurrying the indigo paste into the mixing of the stock and feed baths. Each of the circulation tanks is provided with an agitator, in order to avoid sedimentation of the indigo.

The basic requirements for the operation of the continuous dyeing machine, aside from the chemicals and dyestuffs, are steam and adequate supply of warm and cold water. Each individual bowl is provided with warm and cold water supply inlets. The water utilized in the machines is hard water. The warm water is prepared on the premises in a special heating tank, thermostatically governed so as to deliver at a temperature of about 140° Fahrenheit.

Capacity of the two dye vats is 1,500 gallons each and the oxidizing and rinsing bowls have a content of 900 gallons. The immersion time for the wool in the dye bowls is 6 minutes, in the oxidizing bowls 3 minutes and approximately one minute in the wetting out and rinse bowls. The temperature is kept between 130-135°F. in the dye vats, 120°F. in the oxidizing and rinsing bowls and 140°F. in the wetting out bowl. The function of the dye circulating system is an intricate process. The actual dyeing of the material is accomplished in the second and fifth bowls. As has already been mentioned, the depth of the final shade of the dyed wool is a variable dependent upon the number of dips, on the proper oxidation, the immersion time of each dip and the concentration of the vat liquors. In the continuous train, the number of dips and the immersion time of each dip are fixed so that, in order to make an adjustment upon the shade, the concentration of the vat liquors must be changed. The circulatory system utilized in the continuous train is designated to circulate and replenish the vat liquors continuously as well as distributing the various other solutions prepared at the start of a new bath. In regular operation, the vat liquor is pumped from the feeding tank directly to the second bowl.

The regenerated dye liquors enter the dye bowls through an inlet located below the liquid surface in order to avoid the introduction of air. The overflow and squeeze liquors from the second bowl are then pumped from a compartment situated beneath the squeeze rollers to bowl five and then the squeeze and overflow liquors of dye vat five are pumped back to the feed tank for revitalization.

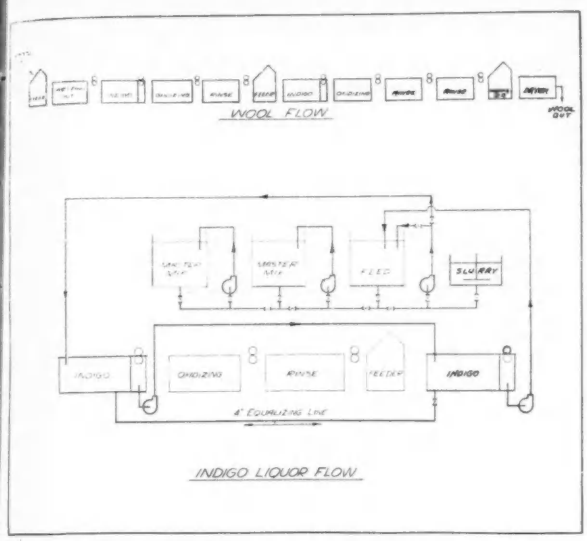
To the circulatory system are added set quantities of known concentration of feed solution which replenishes the circulating liquors with the amount of dyestuff and chemicals removed by the wool and losses in operation. The concentration of feed again depends upon the depth of shade required and the compensation necessary to balance these operation losses. The losses are affected in the carry-over liquor from the dye bowls above the squeeze rollers capacity of removal. The feed or master mix is prepared and held in reserve in the two 1,000-gallon tanks from which it is pumped into the circulatory tank in 25-gallon portions every fifteen minutes.

In starting up with a fresh bath, the spring and stock bath and 1,000 gallons of master mix must be prepared. The total amount of indigo necessary to start the machine is 3,000 pounds. In the first dip, with 6 minutes immersion, the wool takes up 4% indigo (dry basis) which increases to approximately 7½% after the second dip. The two photomicrographs, Figures 2 and 3, illustrate clearly the way the indigo was absorbed and penetrated the fibers.

In the first dip, Figure 2, the main amount of the dye precipitated right after penetrating the epidermis scale. In the second dip, Figure 3, the indigo white was able to penetrate considerably deeper before the oxidation set in the precipitation took place. Still a high amount of dyestuff adheres to the outside of the scale structure and is present right within the epidermis layer, contrary to acid or chrome dyes which generally have no affinity for this layer. The combination of the wool fiber with indigo is purely a physical phenomena. Astbury and Dawson established through X-ray photographs that the indigo in the wool fibers is present in crystallites. Indigo crystals are needle shaped and this gives them a tendency to lie parallel to the fiber axis even in unstretched wool. The negative tippy dyeing of indigo on wool staples is a further proof of its crystalline form. As Speakman and his associates have found, crystalloidal dyes become unlevel owing to the ease with which dye is stripped from the strongly swollen sunlight damaged parts of the staple, resulting in lighter shades on the exposed parts.

Opinions are expressed that the chemical nature of the wool fiber exerts a certain influence in the effect of alkalis and the absorption of the indigo white. The latter substance in the free state exhibit acidic characteristics which would partially explain its great affinity for the wool fiber which is alkaline in part of its chemical reactivity.

That the continuous indigo dyeing produces just as good penetration of the indigo into the fiber as the standard procedure is illustrated by Figure 4 which is a cross section out of a piece of kersey



INDIGO LIQUOR FLOW

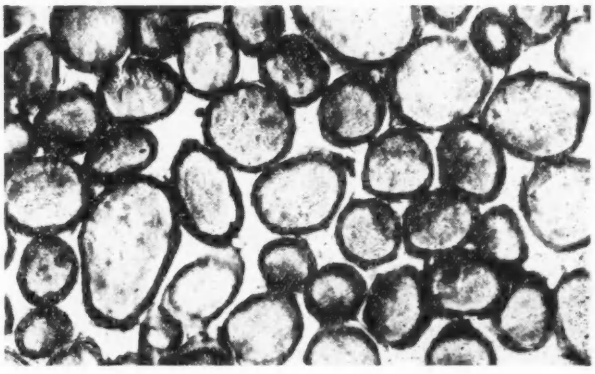


Figure 1 (left).
Figure 2 (above). Cross section of wool after first dip.

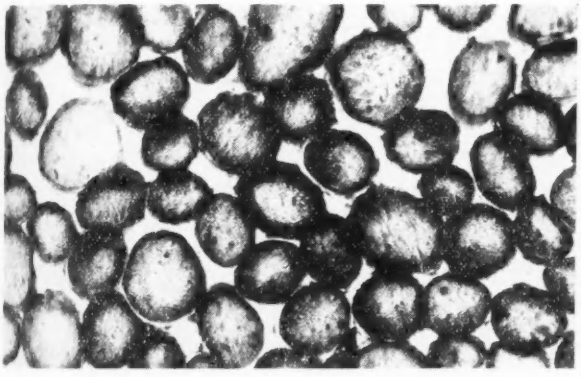


Figure 3. Cross section of wool after second dip.

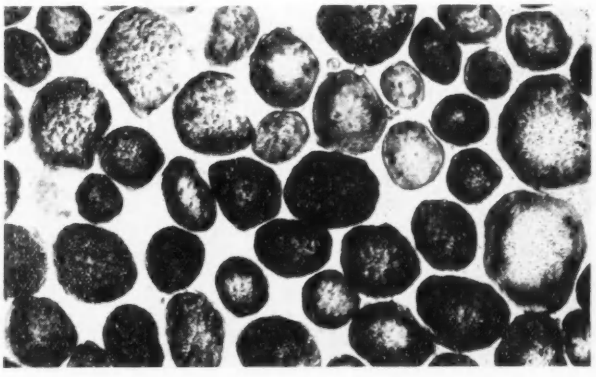


Figure 4. Cross section of wool—chrome bottom, indigo top.

stock dyed the old way, chrome red bottom and indigo top. The same blue ring formations are observed and where the fibers are even dark they show the red cast of the chrome dye.

RESEARCH INVESTIGATIONS OF VARIOUS PHASES OF CONTINUOUS INDIGO DYEING

The continuous stock dyeing process was investigated from a chemical standpoint in order to satisfy a main-fold purpose. Primarily, it was undertaken in order to obtain a clearer insight into the chemical phenomena which are continually influencing the various phases of the dyeing operation.

The process as it is functioning at the present time, has been installed on the basis of similar experience obtained at the Hampshire Woolen Mill and has arrived at its present state of development mainly through the use of trial and error. The effectiveness of this is attested to by the continuous improvement in the efficiency of operation from the outset to the present. At the time of Mr. Wentz departure our quota of wool per dye bath was considered satisfactory with 12,000 lbs. Subsequent experience and improvement in the method has increased our quota to 60,000 lbs. We feel that if this amount could be achieved by purely visual control a much greater quota must be attainable with close chemical supervision.

To the accomplishment of this, the subjects to be studied in order of their investigation were the behavior and characteristics of the wool in the dyeing process, the dyeing liquors and the oxidation baths. These three phases are the main objects of interest from a chemical standpoint in the dyeing operation. In view of the fact that the shade and the condition of the dyed product and the behavior of the wool in the process of being dyed are the most pertinent factors of interest to the dyer and the individuals concerned with the processing of the material through the succeeding manufacturing operations, this aspect of the continuous dyeing process will be considered first.

INDIGO DETERMINATIONS

The most significant factor in the functioning of the continuous indigo dyeing train is the amount of indigo absorbed by the wool and the factors which influence this. In this regard, the most important single factor in the determination of this entity is a suitable and accurate method of estimating the quantity of indigo in the fibrous material.

Indigo is readily soluble in hot pyridine and, therefore, this solubility can be used as a measurement of the color on the fiber. The method as described by Knecht was used after considerable modification. We are still striving to improve and shorten this method, as the entire operation of a single determination requires from 18 to 36 hours. In order to establish the amount of dyestuff and chemicals superficially attached to the wool fibers as the wool emerges from the dye bowl

squeeze rollers, as compared to the amount it contains after the excess is rinsed off in the oxidation and rinse baths, determinations of indigo content were conducted upon samples taken at these points. Six sets of tests were conducted and the average indigo content of the material at the different stages of the dyeing process determined. In Table 2 are tabulated the results of the tests performed.

TABLE 2
Determination of the Indigo Carry-over in Excess Liquor in the Dyed Wool

Test	Per Cent Dry						Ave-
Number	1	2	3	4	5	6	rage
A	3.26	3.70	3.73	4.08	3.83	3.77	3.73
B	3.06	3.41	3.72	3.67	3.32	3.63	3.47
C	6.99	6.94	7.17	6.48	7.09	7.39	7.01
D	6.34	6.77	6.96	6.35	6.59	6.77	6.63

Sample A was produced after the first dip; Sample B, after the first oxidation; Sample C after the second dip and Sample D after the second oxidation.

Average Color Loss, %	
Oxidation 1	0.26
Oxidation 2	0.38

From this study two conclusions can be drawn, namely, that the first dip provides approximately 52 per cent of the total amount of indigo absorbed and that the amount of color lost in carry-over liquor is approximately 10% of that absorbed by the fibers from the dye vat.

The relationship between the dyeing time, the number of dips, wool quality, liquor concentration and the amount of indigo absorption was investigated. The first study conducted was to establish the rate of indigo absorption of wool as a function of time and later as a function of the liquor concentration.

For testing purposes, a 25 meter length of Australian wool top was procured. From this stretch, approximately 10 to 15 gram portions were selected and tied loosely into cheese cloth packages with a length of coarse twine attached to each. The cloth must be packed loosely and openly within the packages in order to achieve even penetration and facilitate dispersal of liquor through the material. Eight such packages were tied together and the cluster immersed for about five minutes in the wetting-out bath. They were then passed through the squeeze roller in like fashion to the rest of the material. The entire cluster of samples was then entered into the first dye vat and the loose end of the twine secured to a part of the mechanism of the machinery to facilitate access to the samples. At each five minute interval, one of the bundles was severed from the rest and drawn from the bath. It was then passed through the squeeze rollers, oxidized, squeezed, rinsed and again squeezed in accordance with the procedure undergone by the regular dyed material. The sample was then removed from the wrapping and dried. Similar treatment was accorded each of the other seven samples which were removed from the bath at five minute intervals from 5 to 40 minutes. The samples were washed thoroughly with soap and water to remove any superficially attached indigo. They were then dried and portions taken for indigo extraction. The relationship between the indigo absorption and time was plotted in Figure 5.

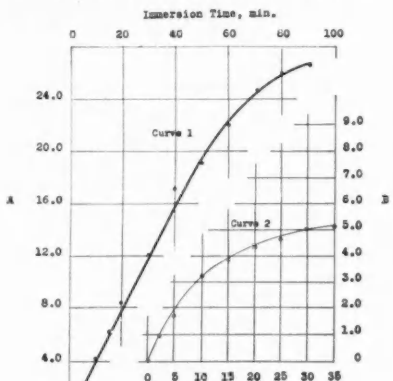


Figure 5. Comparison between the indigo absorption rates with and without intervening oxidation for similar qualities of wool under subjection to identical concentrations of vat liquor. Scales A and B denote the indigo content of the dyed wool at each stage of the testing periods. Each immersion of the material in curve 1 was followed by the regular oxidation and rinse treatment; in curve 2 each sample was permitted the indicated immersion time.

From the appearance of the rate curves, it may be concluded that the rate of indigo absorption in a single dip progresses to an equilibrium point wherein the solubilized indigo solution within the fiber and in the vat liquor are equalized. Naturally this point of equilibrium is variably dependent on the concentration of the vat liquors. The curve shows a sharp incline at the outset, indicating a high rate of absorption which gradually regresses until the point of equilibrium is reached at which point no further color absorption occurs. It is evident that approximately 65% of complete absorption is accomplished during the first 10 minutes of dyeing time; 20% in the next 10 minutes, and 15% in the final 20 minutes. From a dyeing production standpoint the efficiency of color absorption with regard to dyeing time is a significant factor. As the dyer is most interested in achievement of maximum exhaustion of his color so as to derive most efficient utilization of his dyestuff, this point is of considerable significance.

Further tests were conducted in order to discern the saturation point of indigo absorption of the wool fiber. From the above quality of wool top, approximately two meters were taken and wrapped loosely into a cheese cloth package. The wetted-out parcel was then introduced into the dye vat and immersed therein for a four minute interval, at the end of which it was withdrawn and passed through the squeeze roller. After this, it was submerged in the regular peroxide oxidation bowl for a two minute interval, then squeezed and rinsed. The package was then opened and a small portion of the top sample removed. The remainder was re-packed in the cloth and subjected to another dip of five minutes duration as the first immersion. The oxidized and rinsed sample was opened and another small portion removed. The identical procedure was continued and then material subjected up to ten dips with intervening oxidation and with a total immersion time of about 80 minutes in the dye liquors. The samples procured at each phase of the dye train were soaped thoroughly and dried and portions taken therefrom for indigo extraction. The extractions were consummated in accordance with the regular procedure. The results of the extractions are contained in Figure 5 in which comparison may be made between the amount of color absorption with and without intervening oxidation in the identical concentration liquors. As may be seen from the results of these tests on the saturation point of the wool with regard to indigo absorption that a leveling in the rate of absorption is attained at about 26% by weight. The difference in the absorption rates with and without oxidation is emphasized. At fifteen minutes, nearly 70% more color is taken on by the fibers with the intervening oxidation than without it in a single dip; at 30 minutes, the difference is nearly 120%. Naturally the oxidation between dips serves to fix the solubilized indigo so that when the material is re-immersed in the vat liquor, it may again seek equilibrium between the internal and external liquor concentrations with respect to the wool fiber. The fixed dyestuff already deposited within the fibrillae acts more or less inert to the further absorption. It is, therefore, only when the saturation point is attained that no further dyestuff may be forced into the fiber. It was noted in visual inspection of these samples of extremely high indigo content that as the indigo content of the material increases, the material takes on the reddish, bronzy caste, characteristic of the indigotine compound itself. Furthermore, when the indigo content of the material exceeds 8%, considerable difficulty is encountered in detecting the darker coloration in other respects than the passing to the red side.

As a part of the regular control testing of shade depth, samples are procured of the rinsed wool after the first and second

dips by the supervisor in charge of the dye train. These samples are dried, carded and small felts made. The sample is then compared to a standard sample of the desired depth of shade. From each dye bath an average composite sample is selected of the entire production for the effective life of the bath and tested for average indigo content by pyridine extraction as described previously. This testing is performed upon the material after each dip.

The results of these tests conducted upon different percentage dyeings indicate that the results obtained on a production basis are slightly higher than those encountered experimentally. This may be explained by the fact that the top dyed in the experimental studies was packed in cheese cloth parcels, which did not permit the liquors to penetrate and contact the fibers as closely as in the case of the wool dyed in the loose form. However, the theoretical curves illustrate clearly that the rate of absorption of dyestuff is a function of the time of immersion to which the material is subjected and should be governed by the point of maximum absorption.

TABLE 3
Indigo Content of Wool Dyed Under Different Bath Concentrations

Bath Number	Dyeing Per cent	Dyeing Time, hrs.	Indigo Content (Dry Base) Dyed Wool Per cent Dip 1	Dip 2
49	42	45	4.1	7.1
50	42	44	4.3	7.2
51	40	55	4.2	6.9
52	42	31	4.5	7.1
53	42	47	4.6	7.2
54	42	53	5.1	8.0
55	40	99	5.1	7.5
56				
57	45	40	5.3	7.8
58	45	30	4.4	7.1
59	42	46	4.5	7.1
60	42	43	4.6	7.5
61	42	66	4.0	6.5
62	42	54	4.5	7.7
63	42	59	4:5	7.7
64	42	65	4.1	7.2
65	42	60	4.4	6.9
		Average	4.5	7.3

Table 3 substantiates the statement made previously regarding the depth of shade procured in the first and second dye bowls. The first bath delivers approximately 60%, whereas the second bath adds approximately 40% of the total shade required.

Further indigo extraction tests were conducted in order to observe the color loss in the indigo material throughout the various manufacturing processes. Routine indigo determinations were performed periodically upon the finished fabrics as a control check upon the manufacturing processes. Several tests were carried out upon the material in the yarn as well as the raw state.

Indigo determinations upon yarn and raw fabrics must first be preceded by ether extraction to affect the removal of spinning oils which are sprayed upon the stock prior to the carding operation. The samples were then reduced to the oven dry state, weighed and extracted with pyridine. Comparison of the indigo content of the material at various phases of the manufacturing processing is contained in Table 4. The results indicate the loss in color to take place in the finishing operations, such as fulling, scouring and dry cleaning. Despite seemingly high color loss in these processes, the actual loss indicated by pyridine extarction between the stock dyed and finished state averages only approximately 0.5%.

TABLE 4
Indigo Content of Material at Various Stages of the Manufacturing Process

Manufactured State	Indigo Content, % Dry Base
Dyed Stock	7.0
Yarn	7.0
Raw Fabric	7.0
Finished Fabric	6.5

CHEMICAL CONTROL OF DYE LIQUOR

The next phase of the continuous indigo stock dyeing process to be considered are the dyeing liquors themselves and their behavior throughout the dyeing. Due to the complexity of the baths, the high concentration of the constituents, the dense coloration and the sensitivity of the solubilized indigo to the atmospheric oxygen, the development of a suitable testing technique to enable the examination of the liquors is a difficult proposition.

INDIGO CONTENT

One of the most important considerations in dealing with the vat liquors is the indigo concentration therein. The amount of indigo present in the bath is fixed by the initial charge in the stock bath which is diluted by the addition of the spring bath and the required volume of water to satisfy the capacity of the circulatory system. A certain concentration must be maintained throughout the effective life of the vat by the addition of the concentrated feed solution. Due to the complexity of the vat solutions, the determinations of the indigo content in the presence of the multiplicity of chemical reactions by titration methods is extremely difficult. For this reason a rapid technique for gravimetric determination was devised, based upon the principle of the precipitation of the indigo present in the measured volumes of liquor and weighing the resultant indigo. The precipitation was accomplished by a reversal of the chemical equilibria in existence within the dye vats, i.e., a neutralization of the alkali maintaining the buffer and affecting the solubilization of the indigo white by the addition of excess acid and nullification of the reduction potential by the addition of excess oxidizing agent.

Tests were conducted upon the vat liquor from different parts of the circulatory system primarily to ascertain the reproducibility of the results by this testing technique and, secondly, to observe the variations within the circulatory system itself. Samples were selected at the forward end of each dye bath and at the rear of the same as well as from the circulatory tank to which the additions are incorporated. In Table 5 are represented the results of tests performed upon samples drawn from the same bath at different times and tested in quadruplicate in order to verify the reproducibility of the testing procedure.

TABLE 5
Variations in the Indigo Concentration Between Test Specimens

Test Number	*Indigo Content, grs./liter 1*	*2*	*3*	*4*	*Average*
1	3.48	3.02	3.72	3.76	3.49
2	3.02	2.46	2.98	2.84	2.82
3	2.84	2.76	2.88	2.88	2.84
4	3.00	3.00	3.18	3.12	3.07
5	5.52	4.72	4.92	4.66	4.95

The variations encountered in the indigo content of the vat liquors reflect the exact pattern of the dyeing procedure. Naturally then, the concentration of indigo in the circulatory tanks, wherein the additions of feed are introduced would be the most concentrated. Similarly, in each of the dye bowls, the regenerated liquor is entered at the front end of the bath so that it is reasonable to presume that the indigo content of the liquors of this point of the cycle will be higher than at the other end of the bowl where the liquor has been exhausted slightly due to the absorption of the fibers. Table 6 contains the results of various determinations upon samples selected from the different sections of the circulatory cycle at the same time in order to obtain an insight into variations present in the circulatory system. In this test run both dye vats were fed simultaneously.

The next phase of this investigation was the behavior of the indigo content of the bath throughout a single run, as compared with the hypothetical starting charge and feed additions. The procedure outlined above was applied and samples secured at certain intervals and tested for indigo content. Duplicate determinations were performed upon each sample and the results recorded in Figure 6.

It will be noted from the graphical representation of the behavior of the indigo content of the liquor that at the outset a concentration of approximately 7 grams per liter exists in the dye bath which recedes to about 50 per cent of this figure during the first 20 hours of production. Thereafter the indigo concentration remains at that level consistently for the duration of the bath. The starting figure is verified very closely when the constituency of the initial dye bath is considered.

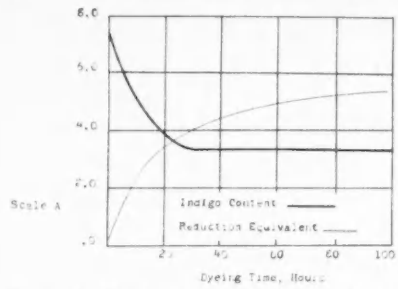


Figure 6. Comparative rate of formation of reducing buffer salts and indigo content of the vat liquor throughout the period of effectivity. Scale A denotes the indigo concentration expressed as grams per liter and reduction equivalent expressed as grams of oxygen required per liter of vat liquor.

REDUCING SALTS

The second phase of the liquors investigated was the amount of reducing strength contained therein. In view of the complexity and multiplicity of intermediate factors within the baths, an estimation of the concentration of each would be extremely difficult. However, in order to obtain a general idea as to the total reducing potential present in the bath, the principle applied in the oxidation of the dyed material was resorted to. In other words, the strength of the bath with regard to total salts was measured by the amount of oxygen that was necessary to counteract the reducing potential. The material was clarified centrifugally by the addition of concentrated acid which affected the neutralization of the alkali salts existing therein. The supernatent liquid which contained the excess oxidizing agent was then titrated iodimetrically with thiosulfate to ascertain the amount of the standard oxidizing capacity utilized to balance the reducing buffer.

Titrations were conducted on the bath liquors throughout the effective life of the dye bath. It must be remembered that this titration represents the composite reducing power of the leuco indigo, excess hydrosulfite, salts formed as a result of the dyeing reactions, such as thiosulfate, bisulfite, sulfites, bisulfates, etc. The studies were performed throughout the life of several baths until the shade depth of the material fell below the prescribed limits markedly and did not respond to the customary chemical additions. The liquor samples were taken from the first dye bowl at a point which approximated the center of the circulatory system. The results of the examination of one bath throughout its effective life are tabulated in Table 7. These tests are also represented graphically in Figure 6.

As may be seen from the rate of formation of these salts, the concentration of them builds up at a fairly regular progression to a certain point. The termination of effectiveness of the dye bath is approached when the liquor needs approximately 8 grm. of oxygen per liter.

TABLE 6

Variations in the Indigo Concentration at Various Localities in the Circulatory System

Test Number	*Indigo Content Grs./Liter A*	*B*	*C*	*D*	*E*
1	7.9	6.8	7.5	6.5	8.1
2	4.9	4.2	4.7	4.4	5.3
3	3.5	2.8	3.1	2.8	4.9
4	3.6	3.0	3.3	3.0	4.7
5	2.3	2.0	1.7	1.8	2.5
Average	4.4	3.7	4.0	3.7	5.1

Note: Figures in Table 6—A indicates the sample was procured at the beginning of the bowl 2; B, at the end of bowl 2; C at the front of bowl 5; D at the end of bowl 5; and E in the circulatory tank.

TABLE 7

Analysis of Dye Liquor Throughout the Effective Life of Dye Vat

Test Number	*Dyeing Time hrs.*	*Reducing Power g O2/L*	*Indigo Content gr./liter*	*pH*
1	2	1.2	7.6	10.0
2	5	1.4	6.8	9.9
3	7	1.7	5.5	9.8
4	11	1.8	5.4	9.6
5	15	2.2	4.8	9.5
6	19	2.3	4.2	9.7
7	21	3.2	4.1	9.7
8	23	3.3	4.0	9.8
10	27	3.4	3.8	9.8
11	28	3.5	3.7	9.8
12	32	3.9	3.8	9.8
13	54	4.2	3.5	9.7
14	56	4.4	3.4	9.7
15	70	4.5	3.6	10.0
16	75	4.9	3.5	10.0
17	85	4.9	3.6	9.9
18	89	5.0	3.5	9.9

ALKALI

From the discussion of the reducing concentration of the vat liquors it may be seen readily that the behavior of the reducing buffer salts are inseparably linked with the alkali concentration. The influence of the caustic soda in dissolving the indigo compound has already been considered. Beside this, the caustic soda, in addition to the soda ash, plays a vital part in maintaining the oxidation products of the hydrosulfite under control.

A study was conducted in order to measure the alkalinity of the dye vat liquors at the outset and throughout the effective life of the bath. The factors which are of interest in this regard are the total alkali, free alkali, carbonates and bicarbonates. A titration technique was devised for the determination of the alkali content of the liquors rapidly and accurately. The volume of acid utilized in the titration of hydroxyl, carbonate and bicarbonate ions was determined in accordance with the ratio elaborated in Table 8.

The total alkalinity of the baths is calculated on the basis of the two MO endpoint and the percentage of the constituent alkalis determined as indicated. In order to observe the behavior of the total alkali throughout the effective life of the dye vat, alkali determinations were conducted during an entire run at regular intervals. The shape of the curves varied with the ratio between the hydroxyl, carbonate and bicarbonate ions. In Figure 7 are contained the variations in the potentiometric curves throughout the run of the dye vat.

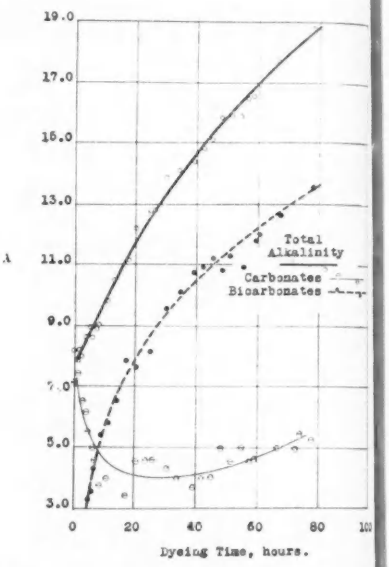


Figure 7. Reference curves for comparison of the ratio of each of the alkali components of the vat liquors throughout the life of the bath. Scale A indicates the alkalinity of each component and the total alkalinity on the basis of sodium oxide (Na_2O), grams per liter of liquor.

In analyzing the vat liquors throughout their period of effectiveness, it was noted that no free alkali exists therein, except at the outset up to the 1½ hours of operation. However, the curved illustrate that the addition of caustic soda from time to time functions to react with the bicarbonate with the maintenance of a positive carbonate concentration. The rates of formation of these components recorded in Figure 7 indicates the continuous building up of the total alkali with the coincident increase in the bicarbonate concentration; whereas, the carbonate concentration remains virtually at a constant. Maintenance of this carbonate concentration, however, is mandatory to effective operation, for once it no longer exists the building-up of bisulfite commences.

The pH results in table 7 show clearly the very slight variation which occur when control is maintained. Remembering the high alkali content by weight with which the bath is started it is remarkable that the pH readings fall in this low range. This phenomea is directly attributed to

the close theoretical calculation of the caustic soda in relation to the indigo to be dissolved and the salts to be controlled. Damage to the wool fiber at this pH is quite remote, viz. wool scouring, if excessive submersion time is refrained from.

OXIDATION

Final consideration in the studies on the continuous stock dyeing process was accorded to the oxidative process by which the solubilized indigo absorbed within the interstices of the fibers is reconverted to indigo blue. As previously mentioned, the oxidation must be effected after each dye dip and it must be accomplished rapidly and completely through the use of chemical oxidation agents. The immersion time of the material in each of the oxidation baths is approximately 1½ minutes. If the wool is entered into the oxidation bath in which the available oxygen concentration is too low, the solubilized indigo within the fibers may be rinsed out before it has the opportunity to become fixed. The stripping action thus affected, naturally, alters the depth of the shade of the final product.

Experience has taught us that regardless of control the carry-over from previous bowls is sufficient to warrant our dropping the oxidizing bowl every 4 hours. To visually understand this we submit Figure 8.

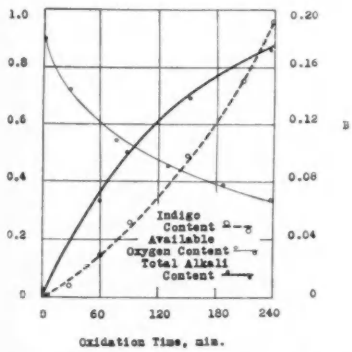


Figure 8. Comparative rates of increase of the available oxygen, total alkali and indigo blue concentration of the peroxide oxidation bath. Scale A denotes the total alkali and indigo content in grams per liter. Scale B denotes the available oxygen concentration in grams per liter.

In obtaining information for the aforementioned chart the methods previously discussed were utilized.

MANUFACTURING PROCESSES

The spinning and weaving operations afforded no difficulties other than the traditional indigo trade-mark-smearing. In the finishing department the most difficult obstacle to overcome was the excessive crocking which appeared after shearing.

TABLE 8

Determination of the Nature of the Alkali Content of the Vat Liquors

Ions	P — O	P — ½ MO	P < ½ MO	P > ½ MO
Hydroxyl	—	—	—	2P — MO
Carbonate	—	MO	2P	2 (MO — P)
Bicarbonate	MO	—	MO — 2P	—

TABLE 9

Differences in Breaking Strength of Yarns and Pieces for 30 Oz. Kersey Using Different Blends and Dyed by Different Methods

Wool Blend: 64's	*25% Australian 25% Cape 50% 12 Mos. Texas*			*100% Cape*		*100% 12 Mos. Texas*	
Dye Process:	*Natural*	*100% Chrome*	*50% Alogosol 50% Chrome*	*100% Chrome*	*100% Indigo*	*100% Indigo*	
Yarn 2.5 Run							
Breaking Strength	185	147	134	161	186	173	
Per cent	100	79.5	72.5	87	100.5	93.5	
Elongation	29.7	20.8	19.2	19.8	27.1	32.2	
Per cent	100	70	64.5	66.5	91	108.5	
Pieces:							
Breaking Strength							*Navy Specifications*
Warp	112	81	102	98	121	113	90
Per cent	100	72	91	87	108	101	
Filling	98	73	89	98	113	98	80
Per cent	100	74	91	100	115	100	

A very careful washing after fulling with subsequent washing in the neutralizing process and a run through the Derby Dry-cleaning machine after shearing remedied the situation. Our present crocking reflection of 80 per cent which is equal to Munsell 8 is evidence that this is correct.

Figure 9 illustrates our standard for crocking control. In order for the pieces to maintain our standard they must cast a reflection above 85 per cent after the fulling wash. The most beneficial attribute to this dye method is the outstanding preservation of the wool fiber. The breaking strength is far above the Navy specification even with 100 per cent domestic wool. The following strength table (Table 9) which draws comparisons between different wool blends and various dye methods experimented with for the manufacturing of the 30 oz. Kersey illustrates the high reward we received for all the hardships encountered..

CONCLUSION

The summation of the technical information as obtained from our analysis of the continuous dyeing of wool with indigo is as follows:

The depth of shade as specified by the Navy Department can be acquired by 2 dips of 6 minutes duration of each.

In the dye liquor the most favorable indigo concentration is 3 grams/liter dry basis or 15 grams of indigo 20 per cent paste. The completely dyed fiber maintains an indigo content of 7 per cent of which 60 per cent is attained in the 1st dip and the remaining 40 per cent in the 2nd dip.

The efficiency of the bath and the duration of its effectiveness is entirely dependent on the control of the accumulation of the various chemicals which in turn are necessary for indigo dyeing. The oxidation products of sodium hydrosulfite accumulate and build up continuously and upon reaching an equivalent of approximately 8 grams of oxygen/liter the effectiveness of the dye bath is terminated.

The caustic soda and the sodium carbonate in reacting with the oxidation products of the hydrosulfite lead to the formation of sodium bicarbonate. The entire reaction is a continuous cycle. The total alkali builds up to approximately 20 grams per liter during a 90 hour run with the coincident increase in the bicarbonate concentration. Maintenance of a certain carbonate concentration is mandatory to effective operation.

The manufacturing loss of actual indigo though it appears excessively high is actually a mere ½ per cent.

The continuous stock dyeing of wool with indigo has left the realms of wishful thinking and has become a practical reality with a production of approximately 3,000,000 pounds of wool dyed during the past 12 months. The decision of the Forstmann Woolen Co. to construct the necessary equipment for this process and to carry on the careful experimentation that was required before successful operation was achieved, is one of the major contributions of the textile industry to the war effort. It has made available to the United States Navy the production of indigo dyed fabrics with all the color advantages of stock dyeing without loss of strength or fiber damage and has coupled with this the further gains of high production efficiency and definite savings in manpower required.

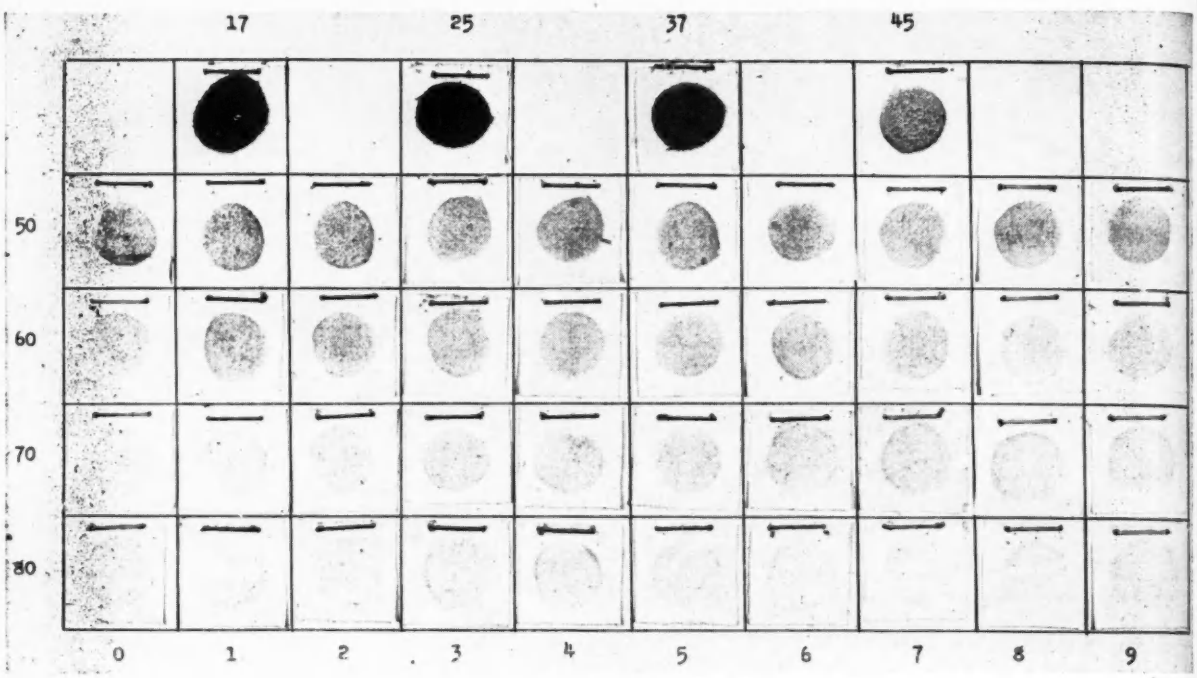


Figure 9. Indigo Crocking Standards—Percentage Reflection

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DISCUSSION

Chairman Harris: Thank you, Mr. Von Bergen.

I have taken the liberty of asking John Dalton of the Pacific Mills to make a number of comments on Dr. Von Bergen's paper.

John N. Dalton: I haven't very much comment to offer. From reading the paper, it seems to me to be a very excellent presentation, very complete. In fact, I couldn't see but what most of the questions that might be answered were covered.

I did receive one very excellent impression from this work, and that is that in addition to the objections which the Navy Department might have had to chrome dyeing, one of the features of the indigo dyeing is that you get a stronger fabric which would enhance using indigo in dyeing for Navy requirements.

There is one thing I want to mention. The paper, of course, contains a great deal more detail than Dr. Von Bergen had time to give here. However, I think it would be interesting if you would comment on the theory of why indigo penetrates the dyed wool at the low temperatures in contrast to the usual high temperatures necessary for acid dyes.

Mr. Von Bergen: According to Astbury, the indigo is precipitated in the wool fiber in crystalline form, so actually it is more or less a physical phenomenon. As you saw it, it entered mainly the outside ring of the wool fiber epidermis, whereas in regular chrome or acid dyeing that seldom happens. Actually, as soon as the dyestuff is through the epidermis scale, it settles on the cuticle layer. The epidermis layer has generally no affinity for regular acid and chrome dyes.

Dr. Hans Luttringhaus: In the cross sections on the slides, you showed oxidized indigo and unoxidized indigo. Can you tell me, please, how you took the picture of the unoxidized indigo?

Mr. Von Bergen: That is a very good question, gentlemen. It was the dream of my microscopist to make such a picture. I told him, "Try and do it." Accidentally, he did it. We worked with the new Ansco color film. The first exposure he made of the first dip was quite overexposed and produced the green yellow color of unoxidized indigo. So I said, "We will show it to the people and see how many will realize that it is trick photography." (Laughter)

Dr. Luttringhaus: There is another question. You just stated that indigo is fixed on the wool fiber in crystalline form. You mean that it is simply precipitated?

Mr. Von Bergen: Yes.

Dr. Luttringhaus: Binz and Mandowsky have carried out interesting experiments with sodium alcoholate which seem to prove that indigo is chemically bound to the fiber. If you treat a blue dyeing of indigo with sodium alcoholate, you do not get a reduction, while you get a reduction with indigo as such.

Chairman Harris: I think it ought to be pointed out that the x-ray patterns could show crystals having formed in there after the dyeing having taken place, and you only have to have minute cross quantity. Actually, the bulk of the process would be a chemical one. You wouldn't have to have a crystalline dyeing to get some defraction in your x-ray pattern from small crystals of indigo in the fiber.

Dr. Luttringhaus: By the way, the crystallites do not necessarily contradict this; that is, the outside of the crystallites might still be chemically attached to the wool.

Chairman Harris: Well, I think it is better conceivably, and I think there is some evidence that a molecule can at-

each itself some place to the wool and form a crystallite at that point.

Dr. Luttringhaus: That is what I mean.

Chairman Harris: That is correct.

Dr. Luttringhaus: You drop the oxidizing bath after four hours. That is understandable because of the accumulation of alkali and indigo. Would it be possible to use the bath for a longer time if the amount of peroxide would be increased in spite of the accumulation?

William F. Brommelsiek: Let me explain the main reasons for dropping our bath after four hours. It was not only due to contamination, but also because the War Production Board continuously tightened up our allocated amount of peroxide. We found out that the amount of peroxide required to maintain an operation equilibrium of oxygen after four hours was atrociously high.

Not only these reasons, but the dyeing price also rose. Naturally, the accumulation of extra Indigo in the oxidizing bath settled on the fiber, and was carried into our second indigo bath. After the second indigo bath, if it did not damage that too much, it was carried on and remained on the fiber which increased the crocking. Therefore, we discovered that after a four hour run in the oxidizing bath, if we dropped the liquor and started with fresh water and chemicals, we could obtain the better crocking fastness and also save an abundance of peroxide, which was our main intent.

The remainder of the papers presented at the Wool Group Meeting will be published in the next issue.

ONE HUNDRED AND FORTIETH MEETING OF THE RESEARCH COMMITTEE

CONTRARY to usual custom, the 140th meeting of the Research Committee, on Friday morning, October 13, 1944, was open to all members and guests attending the General Meeting of the Association in the Hotel Claridge, Atlantic City, N. J. Chairman Louis A. Olney, presiding, first introduced Leonard S. Little, Chairman of the Executive Committee for Research, who reported that this committee had met within a year in New York City four times, and in Washington, D. C.; Greenville, S. C.; Lowell, Mass., and LaGrange, Ga. Its annual budget for research had increased to $20,000.

Dr. Henry D. Barker, reporting for the Committee on Mildew Proofing, stated that fabrics treated with three different fungicides, in three concentrations, had been distributed among several laboratories for trial of tests. The Quartermaster Corps of the Army meanwhile was sending prepared fabrics to the tropics for correlation of tests with field conditions. Charles W. Dorn, reporting on Wash Fastness Tests for Dyed or Printed Textiles, described large scale distribution of cotton samples for laundering, and subsequent correlation of results with revised laboratory tests. Miss Mary P. Shelton showed samples illustrating details of the work. Similar studies were being planned for hosiery by Henry B. Dixon, and for rayon by Arthur R. Wachter. George A. Slowinske and Bertil A. Ryberg described progress on comparative tests of the Association's hydrostatic pressure tester and the Suter tester. Mr. Slowinske emphasized the fact that neither these nor other instruments thus far tested by the Association really simulated rain, so that machines for this purpose would involve further investigation. Olen F. Marks and Mr. Ryberg described the machine devised for study of Dimensional Changes of Fabrics, and progress of test development under the American Viscose Scholarship.

Mr. Prisley outlined plans of the Committee on Detergency for investigations on cellulose and synthetics under V. B. Holland, and wool under C. L. Nutting. Major Stiegler reported for the Committee on Crease Resistance and Permanancy of Finish, and H. W. Leitch for the Committee on Chemical Technology of Wool. Dr. Ruby K. Worner of the Committee on Bibliography asked for assistance on foreign journals. Mr. Christison reported that the new light fastness standards were completed, but not ready for general distribution until tested by several laboratories. Mr. Redmond reported on Testing Fire Resistant Material, and Professor Grimshaw on Standard Methods of Chemical Analysis and Testing. Dr. Draves asked assistance in trial of the new Rewetting Test by laboratories equipped with temperature and humidity control. He reported progress on a new test for wetting out in mercerizing baths. A written report was read, from W. C. Durfee, on Fastness to Rubbing. The Chairman showed the new multifiber fabric, reporting that all thus far in production had been sold.

Respectfully submitted,
Harold C. Chapin, *Secretary*.

CORRECTION

Re: Use of "Bemberg"

It has been brought to our attention that the registered trademark "Bemberg" was misused in the paper "Effect on the Appearance of Hosiery Made from Viscose, Bemberg and Acetate Yarns Subjected to Variations in Tension and Steaming During Throwing" which appeared in our December 4th, 1944, issue. The word "Bemberg" was printed without a capital letter and erroneously used in a generic sense without proper trademark notice. "Bemberg" is the registered trademark of American Bemberg Corporation designating cuprammonium cellulose yarn made by the Bemberg process.

MEETING, SOUTH CENTRAL SECTION

THE December meeting of the South Central Section was held at the Patton Hotel in Chattanooga, Tennessee, on Saturday, December 9, 1944. There were 70 visitors and members present.

John R. Berwick of the Sandoz Chemical Co. presented a paper on "The Metachrome Dyeing of Wool."

G. M. Cooper of the Dixie Mercerizing Co. gave the highlights of his paper, "Cotton Knitting Yarn—Factors Influencing Its Knittability," which he presented in the Intersectional Contest in Atlantic City.

The election of officers for 1945 was held and the following were elected:

Chairman, Frank F. Myers, Geigy Co., 700 Belvoir Ave., Chattanooga, Tenn.

Vice-chairman, W. P. Clements, Kingsboro Silk Mills, Daisy, Tenn.

Secretary, W. K. Newman, Peerless Woolen Mills, Rossville, Ga.

Treasurer, G. R. Bellamy, Ciba Co., 1008 Forrest Ave., Chattanooga, Tenn.

Councillor, E. H. Dobbins, The Trion Co., Trion, Ga.

Sectional Committee: Jack Anderson, Peerless Woolen Mills, Rossville, Ga.; R. W. Freeze, American Aniline Products Co., 2202 Chamberlain Ave., Chattanooga, Tenn.; A. J. Kelly, Burkart-Schier Chemical Co., Chattanooga, Tenn.; W. S. McNab, Quaker City Chemical Co., Knoxville, Tenn.

Respectfully submitted,
W. K. Newman, *Acting Secretary*.

MEMBERSHIP APPLICATIONS

SENIOR

Dwight F. Allen—Chemist, Clearwater Manufacturing Co., Clearwater, S. C. Sponsors: J. E. Truax, T. Larson.

Carl N. Anderson—Research Director, Puritized, Inc., New York, N. Y. Sponsors: H. C. Borghetty, E. C. Hansen.

Tully H. Babb—Chemist, Asst. Dyer, Pacific Mills, Lyman, S. C. Sponsor: R. E. Rupp.

Ladislaus Balassa—Director of Research, U. S. Finishing Co., Norwich, Conn. Sponsors: W. H. Cady, M. F. Davis.

Photo taken at meeting of New York Section on November 17th, 1944. The report of this meeting was published in our issue of December 18th, 1944.

Morry A. Bard—Secretary & Treas., Silverline Dye Works, New York, N. Y. Sponsor: L. J. Dogin.

Alfred A. Beckwith—Vice President, Textile Service & Chem. Corp., North Quincy, Mass. Sponsors: A. E. Raimo, H. B. Dohner.

August Berlings—Head Dyer, Tubize Rayon Corp., Hopewell, Va. Sponsors: W. B. Carroll Jr., B. S. Bellemere.

Robert T. Berry—Dyer, Olson Rug Co., Chicago, Ill. Sponsors: F. J. Ackert, A. J. Olson.

Gavin T. Binner—Head Dyer, Blue Ridge Woolen Co., Chambersburg, Pa. Sponsors: A. E. Raimo, A. W. Edwards.

Donald A. Bishop—Asst. Supt. Synthetic Products Div., Arnold Hoffman & Co., Dighton, Mass. Sponsors: E. D. McLeod, I. W. Fallstrom.

Charles E. Bloom—General Mgr., Fidelity Chemical Products Corp., Newark, N. J. Sponsors: A. E. Raimo, W. F. Fancourt, 3rd.

E. Franklin Bohl—Asst. Plant Mgr., Eastern Piece Dye Wks. Div. National Dyeing & Printing Co., Allentown, Pa. Sponsors: F. H. Riale, J. Niewaroski.

Edward M. Bradley—Demonstrator, National Aniline Div., Allied Chemical & Dye Corp., Buffalo, N. Y. Sponsors: T. F. Murphy, M. A. Cullen.

William J. Brink—Technician, Leather Chemical Co., Philadelphia, Pa. Sponsors: A. E. Raimo, J. F. Rieder.

Donald W. Buehler—Fancy Dyer, Kramer Corp., Milwaukee, Wis. Sponsors: A. G. Alexander, A. H. Kranstover.

H. William Buisson—Colorist, Andrejkovicz & Dunk, Inc. Philadelphia, Pa. Sponsors: C. Baeringer, A. E. Raimo.

Dana Burks, Jr.—Research Chemist, Kendall Mills, Walpole, Mass. Sponsors: L. S. Little, P. J. Kennedy.

CALENDAR OF COMING EVENTS

Meeting, Rhode Island Section, Providence Engineering Society Hall, 195 Angell Street, Providence, R. I., February 23, 1945.

Meeting, Philadelphia Section, February 23, 1945.

Meeting, Northern New England Section, March 16, 1945

Meeting, New York Section, Downtown Athletic Club, New York City, March 16, 1945. Symposium on "Recent Developments in Finishing and their Application to Fabrics." Speakers will be Capt. Goodavage and Messrs. Ackley and Nute.

Meeting, Council, Providence Engineering Society Hall, 195 Angell Street, Providence, R. I., March 23, 1945.

Meeting, Research Committee, Providence Engineering Society Hall, 195 Angell Street, Providence, R. I., March 23, 1945.

OBITUARY

ERNEST BARBER

ERNEST BARBER, textile consultant, died at his home, 150 Graham Avenue, Paterson, N. J., on January 6th, after a long illness. He was 78 years old.

Mr. Barber was born in Macclesfield, England, and received his early training there in a silk mill, of which his father was superintendent. He came to this country in 1891, and was eventually connected with several leading silk manufacturers. He was a part owner of the Pearson and Barber mill and the Wechsler Barber Silk Company. He later became a consultant.

EDWARD D. KINGSLEY

EDWARD D. KINGSLEY, chairman of the board of the Niagara Alkali Company, died on January 1st. He was born in Williamsburg, Mass., eight-four years ago.

Mr. Kingsley organized the Electro Bleaching Gas Company for the manufacture and distribution of liquid chlorine in the spring of 1907. In 1915 he acquired control of the Niagara Alkali Company, manufacturers of heavy chemicals, and later added the Pacific Lime Company, Ltd., the Kingsley Navigation Company, Ltd. (both of Canada) and the Kingsley Navigation Company of California.

Mr. Kingsley was a member of the Chemists' Club, Niagara Club of Niagara Falls, New York, the American Chemical Society and the Electrochemical Society.

WILLIAM L. PIERCE, JR.

WILLIAM L. PIERCE, JR., associated with the Textile Division of National Starch Products, New York, died of a heart attack at his home in Englewood, N. J., November 22.

Mr. Pierce was prominent in the textile finishing industry for many years. He was first connected with Bellman Brook Bleachery, Fair View, N. J., of which he became vice-president. In June, 1935, he joined the Newburg Bleachery, Newburg, N. Y., and was sales manager of the organization in charge of the New York office until August, 1939. He served as president of the National Association of Finishers of Textile Fabrics during the years 1930 through 1934.

Mr. Pierce was graduated from Princeton University in 1911 and attended Columbia Law School until the outbreak of the first World War, in which he served overseas in the tank corps. He was a member of the Merchants Club of New York, and the Knickerbocker and Englewood Golf Club.

He leaves his widow, two daughters, a brother and a sister.

• TEXCHEM FINISHES

In the listing of new products appearing in our December 4th, 1944 issue, reference was made to "Kilcomines" and "Kilco Terge A." We are informed by the Textile Chemicals Corp. of R. I., 511 Westminster Street, Providence 3, R. I., that these products are now sold under the name "Texchem Finishes."

• SANDOZ RESEARCH DEPARTMENT

Sandoz Chemical Works, Inc., have announced the appointment of Charles H. A. Schmitt to organize and direct a research department. Mr. Schmitt has been affiliated with Sandoz for 15 years, being Technical Manager in the New England area for the last several years. He has visited many textile mills in his technical capacity and consequently has been in close touch with the problems and requirements of the textile field.

Charles H. A. Schmitt

Mr. Schmitt has been an active member of the American Association of Textile Chemists and Colorists for many years: At present he is a councillor representing the Northern New England Section and is a member of the National Research Committee.

The company states that with the establishment of its research department, in addition to the facilities of its long established application laboratories, it can offer a wider and more useful service to the textile industry.

• EVENING TEXTILE COURSES

H. R. Mauersberger, in charge of the Evening Textile Courses at Columbia University, announces that registration for the 1945 Spring Term begins January 31st. The following schedule of courses is being offered in the order of their openings:

Woolen and Worsted Manufacture, by Werner von Bergen, Mondays, begins February 5th, 1945.

Cotton Goods Converting, by John Hagen, Tuesdays, begins February 6th, 1945.

Identification, Analysis and Testing of Textiles, by Gordon R. Turner, Wednesdays, begins February 7th, 1945.

Converting Rayon and Spun Rayon Fabrics, by H. R. Mauersberger, Thursdays, begins February 8th, 1945.

Textile Chemistry, by Ludwig Fusser, Fridays, begins February 9th, 1945.

All courses extend over 15 weeks, one a week, and end on May 25th. They are open to all men and women over 18 years of age. A free descriptive leaflet is available from the Registrar, Columbia University, Extension Division, or phone Mr. Mauersberger at MUrray Hill 4-1159 for specific details and questions.

• APPOINTED HOOKER MANAGER

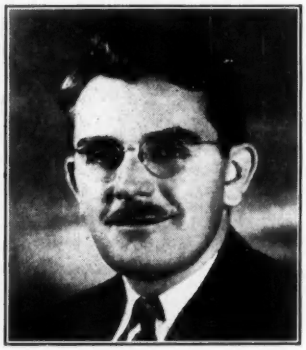
The Hooker Electrochemical Company announces the appointment of John S. Coey as manager of its Sales Development Department at Niagara Falls, New York. Prior to this promotion, Mr. Coey was an assistant in this department. In 1937 he joined the Hooker technical staff

John S. Coey

in charge of the Process Study Group working on the improvement of processes and products. A graduate chemist from Amherst College, Mr. Coey is well equipped to give technical assistance to the chemical industries served by Hooker.

● **JOINS ONYX**

Charles G. Marshall has joined the staff of the Onyx Oil & Chemical Company, Jersey City, N. J., as Director in charge of the Industrial Division. For the past five years Mr. Marshall's efforts have been directed toward the technical and sales development of quaternary ammonium



Charles G. Marshall

compounds in the field of public health. In his new position he has assumed the development of cationic germicidal disinfectants and other associated chemicals. Mr. Marshall was formerly Associate Director of the Industrial Division of Winthrop Chemical Co., Inc.

● **APPOINTED MANAGER, WESTVACO SALES**

Effective November 15, J. C. Thom was appointed Manager of Sales of Westvaco Chlorine Products Corp., New York, N. Y., according to an announcement re-

J. C. Thom

ceived from Louis Neuberg, Vice President. Since August, 1943, Mr. Thom has been Westvaco's acting Manager of Sales succeeding the late J. Rivers Adams.

● **ARNOLD, HOFFMAN APPOINTMENT**

Arnold, Hoffman & Co., Inc., manufacturing chemists, with headquarters in Providence, Rhode Island, announce the appointment of Jeffrey B. Henriques as Vice President in Charge of Purchasing

Jeffrey B. Henriques

and Sales for Arnold-Hoffman Company, their new Industrial Chemical Sales Division.

New offices will be opened on the 51st floor of the Empire State Building, New York, to accommodate both the present manufacturing sales division and the new heavy chemical organization.

For the past twelve years Mr. Henriques has been General Purchasing Agent for the United Merchants & Manufacturers Management Corporation, and is widely known in the trade.

● **ELECTED PRESIDENT, A.A.T.T.**

Carl I. Taber, manager fabric development, Acetate Division, E. I. duPont de Nemours & Company, has been elected president of the American Association of

Carl I. Taber

Textile Technologists. A native of Moosup, Conn., he is a graduate of Brown University and attended the Rhode Island School of Design. Mr. Taber is a member of the American Association of Textile Chemists and Colorists and Phi Gamma Delta fraternity. A Navy veteran of World War I, he joined the Du Pont Company in 1927. He assisted in determining probable uses for acetate yarn in this country prior to the company's entrance into the field in 1929.

● **OFFICERS, PLASTICS CLUB**

The Plastics Club of the United States announces the election of the following officers for 1945:

President, John Owen, Sorg Paper Co. Vice President, Charles Gates, B. Altman Company; Vice President, J. Murray Beveridge, Mavco Sales.

Ephraim Freedman, R. H. Macy & Co. has been elected to the Board of Advisors.

Programs for early 1945 include merchandising demonstrations and talks by E. I. DuPont, the Plaskon Company, and the Celanese Plastics Corp.

● **HONORARY DEGREE FOR DDT RESEARCH DIRECTOR**

Geigy Company, Inc., New York dyestuff house, has received a cable from Switzerland announcing that Basle University has conferred the honorary degree of Doctor of Medicine upon Paul Laeuger, Technical Director of J. R. Geigy, the Swiss parent organization, which brought out the insecticidal properties of DDT. The award to Mr. Laeuger was made for his work in Gesarol, Neocid and other DDT compositions.

● **RHODE CHEMICAL CORP.**

Harold W. Rose, as president, announces the formation of the Rhode Chemical Corporation with offices located at 64-68 Hamilton Street, Paterson 1, N. J. The new company is engaged in the distribution of chemicals, oils and textile specialties. It is also stated that several patented and highly specialized products are being distributed by the company as sole manufacturers' agent.

● **NEW YORK ROHM & HAAS OFFICE**

Rohm & Haas Company of Philadelphia announces the removal of their New York City office to new and larger quarters at 11 West 42nd Street, telephone LOngacre 3-2390. The sale of Plexiglas sheets and molding powders will be handled by D. S. Plume and H. L. Stauffer, who will make their headquarters in the new office.

At the same time, Rohm & Haas also announce that William Torres of Woodbury, Connecticut, will handle the sale of Plexiglas sheets and molding powders in the New England territory together with Harry E. Holmes.

● **NEW GLYCO CATALOG**

The 1945 edition of "Chemicals by Glyco" has just been published, according to the Glyco Products Co., Inc., 26 Court St., Brooklyn 2, N. Y. A number of additional items are described, as well as the usual esters, synthetic waxes, emulsifying agents, etc., manufactured by the company. The contents have been regrouped somewhat to make for more convenient reference.